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PART ONE

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LABORATORY NOTES

FOR A

BEGINNER'S COURSE

IN

QUANTITATIVE ANALYSIS

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## PREFACE TO PART ONE AND NOTICE TO TEACHERS.

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As indicated by the title, the first part of this book consists of Laboratory Notes for a Beginners' Course in Quantitative Analysis. It considers the subjects of Gravimetric and Volumetric Analysis, for beginners, by means of the analyses of a set of substances, properly numbered and arranged in what seems to be a desirable order for study, in each case giving the methods to be followed in each analysis; it also gives the methods to be used in calculating and preparing standard solutions for volumetric work, generally following the course offered by Professor Cheever to his students.

Although a number of the methods of analysis given in Part One may be of only approximate accuracy and of small commercial value, such are yet included with a special purpose, to-wit:—that they may supply the student with a diversity of chemical manipulation, at the same time giving him an early opportunity for the necessary careful selection of the methods which he should adopt. This was Professor Cheever's idea, and it is certainly a good one, especially since, in most cases, the work of the beginner simply serves to emphasize the necessity of careful scrutiny of details and methods for practical work in the future.

Part One is then offered as a complete and well-arranged course for elementary students in schools and colleges; and it is intended that students should exactly follow the arrangement in the book, beginning with the subject of Spe-

cific Gravities, continuing with Gravimetric Determinations, Volumetric Analysis and Gravimetric Separations (with such rapidity as may seem advisable to the teacher) and being supplied by the teacher with samples of material for examination, of which a record is kept, whereby the work of the student may be tested as to its accuracy. The subject matter of the book, as taken in its order, will supply abundant material for class questions.

## SPECIFIC GRAVITY.\*

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The specific gravity of a body is the weight of that body as compared with the weight of an equal volume of a standard body, which is taken as unity. In all cases considering the specific gravity of solids and liquids, this standard of unity is pure water at  $60^{\circ}$  F. =  $15.5^{\circ}$  C. Water being taken as unity, or one, any other substance will be more or less than one. The results are expressed in whole numbers and decimals; the decimals are carried to the third place.

Water = 1.000 (*one, not one thousand*).

Alcohol = 0.815

Sand = 2.127

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### Gravimetric Methods of Determining the Specific Gravities of Solids and Liquids.

Before proceeding with the following operations, *read carefully the Rules for Weighing*, as given in the Appendix.

The student should carefully read the following advice:—*Cleanliness, Patience, and the most careful attention to detail are indispensable in chemical manipulations.*

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The following classification will serve for all solids and liquids which are likely to occur in ordinary investigations:

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\*Watt's Dictionary, Vol. 5, page 357.

1. Liquids, heavier or lighter than water.
  2. Solids, in powder, heavier than water and insoluble in it.
  3. Solids, in mass, heavier than water and insoluble in it.
  4. Solids, lighter than water and insoluble in it.
  5. Solids, soluble in water.
- 

*Class I. Liquids, Heavier or Lighter than Water.*

Take a specific gravity bottle, clean and dry it, cool and weigh. The bottle may be dried more quickly by making the last washing with alcohol.

Fill the bottle with distilled water, at a temperature of  $15.5^{\circ}$  Centigrade, avoiding the presence of air-bubbles about the stopper, and weigh again. If the above weights are carefully obtained, it will not be necessary to repeat them, except in case of accident.

Empty and dry the bottle as before, cool it and fill with the liquid under examination, at a temperature of  $15.5^{\circ}$  C., avoiding air-bubbles as before, and weigh again. We thus obtain the weights of equal volumes of pure water and the liquid under examination, and obtain the specific gravity of the latter by the following calculation:—

If  $B$  = the weight of the specific gravity bottle,  
 $W$  = the weight of the distilled water, and  
 $L$  = the weight of an equal volume of the liquid,  
having obtained the values of  $W$  and  $L$  as follows:  
 $B + \text{Water} = 30$  grams,       $B + \text{Liquid} = 38$  grams,  
 $B = 10$  grams,       $B = 10$  grams,  
 $W = 20$  grams.       $L = 28$  grams.  
we divide the weight of the liquid by the weight of the equal

volume of pure water, thus:  $\frac{L}{W} = \frac{28}{20} = 1.400$ ; which is the specific gravity of the liquid.

*Examples for Practice.*

The student will determine the specific gravity of the following Table Reagents, by the above method, and report the results obtained to the teacher: HCl, HNO<sub>3</sub>, HC<sub>2</sub>H<sub>5</sub>O<sub>2</sub>, KOH, NH<sub>4</sub>OH, C<sub>2</sub>H<sub>6</sub>O.

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*Class 2. Solids, in Powder, Heavier than Water and Insoluble in it.*

Clean, dry and cool the specific gravity bottle as before; put into it from two to five grams of the powder and weigh. Fill the bottle, containing the powder, with distilled water (avoiding air-bubbles as before), and weigh again.

B + Water = 30 grams,	B + Powder = 20 grams,
B = 10 grams.	B = 10 grams,
<hr/>	<hr/>
W = 20 grams.	P = 10 grams.
B + P + Water = 36 grams,	W = 20 grams.
B + P = 20 grams,	W <sub>1</sub> = 16 grams,
<hr/>	<hr/>
W <sub>2</sub> = 4 grams.	W <sub>2</sub> = 4 grams.

W = Weight of the water which the bottle holds.

W<sub>1</sub> = Weight of water above the powder.

W<sub>2</sub> = Weight of water displaced by powder.

The displaced water has the same volume as that of the powder which displaced it, and we therefore have the weight of the powder (P = 10 grams), and the weight of an equal volume of water (W<sub>2</sub> = 4 grams). Applying the rule above given, we have P ÷ W<sub>2</sub> = 10 ÷ 4 = 2.500, which is the specific gravity of the powder.

*Examples for Practice.*

The student will determine the specific gravities of the powders in Boxes Nos. 1 and 2, which have been furnished him, and report the results.

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*Class 3. Solids, in Mass, Heavier than Water and Insoluble in it.*

Suspend the substance from the arm of the balance, by means of a horsehair, and weigh. Place a beaker containing distilled water on the bridge over the scale-pan, so that the suspended substance hangs freely in it, and weigh again; taking care that no air-bubbles adhere to the substance.

The loss in weight is equal to the weight of the water displaced by the substance, or the weight of a volume of water equal to that of the substance; dividing the weight in air by the loss of weight in water, as before, we obtain the specific gravity required.

Weight of Substance in air.....25 grams, = S.

Weight of Substance in water....15 grams,

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Loss of weight in water.....10 grams, = W.

$S \div W = 25 \div 10 = 2.500$ , the specific gravity of the substance.

The student will determine the specific gravity of the substance in Box No. 3, by the above method, and report the result.

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*Class 4. Solids, Lighter than Water and Insoluble in it.*

Such substances, being lighter than water, will not sink in it; hence they must be attached to some heavy substance which will cause them to sink, and thus displace a certain volume of water. For example, take wood.

- (1) Weight of sinker in air..... 50 grams,  
 (2) Weight of sinker and wood in air...183 grams,
- 

Difference = weight of wood in air.....133 grams =  $W_1$ .

- (3) Weight of sinker and wood in water. 38 grams,  
 (4) Weight of sinker in water..... 44 grams,

$$\text{Weight (2)} - \text{Weight (3)} \\ \text{or } 183 - 38 \} = 145 = \left\{ \begin{array}{l} \text{Weight of the water} \\ \text{displaced by sinker and} \\ \text{wood.} \end{array} \right\} = W_1$$

$$\text{Weight (1)} - \text{Weight (4)} \\ \text{or } 50 - 44 \} = 6 = \left\{ \begin{array}{l} \text{Weight of the water} \\ \text{displaced by sinker.} \end{array} \right\} = W_2$$

$$W_1 - W_2 \} = 139 = \text{weight of the water displaced by} \\ 145 - 6 \} \text{wood,} = W_3$$

$W \div W_3 = 133 \div 139 = 0.956$ , the specific gravity of the wood.

The student will determine the specific gravity of the substances in Boxes Nos. 4 and 5, by the above method, and report results.

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### *Class 5. Solids, Soluble in Water.*

Select some liquid in which the solid is insoluble. Determine the specific gravity of the substance in this liquid, by one of the preceding methods, and multiply the result obtained by the specific gravity of the liquid used; the product will be the specific gravity required.

The student will determine the specific gravity of the substance in Box No. 6 by the above method, and report result. The substance will be found to be insoluble in alcohol.

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### **Further Notes On Specific Gravity.**

In taking the specific gravity of chemical compounds, such as minerals, etc., it is obvious that the sample should

be pure or unaltered; otherwise the results obtained may be misleading. A transparent mineral will have a higher specific gravity than will a piece of the same mineral which has many cracks; since the cracks contain air. In case a mineral is porous or earthy, it should be boiled in water for some minutes to expel the air, then allowed to cool in the water to the temperature of the room. The weight in water is then determined. The fragment is then dried and weighed in air. From comparison of these results the specific gravity is obtained. Several forms of balances are well adapted for the rapid determination of specific gravities of many solids. Of these the Jolly balance is much in use.

In determining the specific gravities of liquids, hydrometers are much used, some of them showing the specific gravity direct, and others, such as the Baumé hydrometer, being marked *in degrees*. The liquid to be examined may be an oil which will not flow easily at ordinary temperatures; in this case the oil is warmed till it is sufficiently liquid, the specific gravity taken and the temperature of the oil observed; after which a correction is applied for the temperature, and the Baumé degrees are converted to specific gravity by the Table:—see Appendix.

Knowing the components of a mixture, and the specific gravity of the ingredients, the percentage composition may be approximately calculated as follows:—Let A represent the specific gravity of one ingredient 0.807, and B that of the other ingredient 0.670, and C the specific gravity of the mixture 0.727. Then,  $A - C = D$ , and  $C - B = E$ ;

$$\frac{E}{D+E} = \% A = 41.6 \text{ and } \frac{D}{D+E} = \% B = 58.4.$$

# QUANTITATIVE ANALYSIS.

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## PRELIMINARY STEPS.

(1) *Selecting the Sample*.—The mode of selecting the sample will depend on the object sought. Correct sampling is of vital importance to the value of chemical analysis. In commercial work the sample should be so selected as to represent, as nearly as possible, the average quality of the whole. If the material to be sampled is a solid, this can best be accomplished by pulverizing a large quantity taken from different parts of the mass, thoroughly mixing the same and again sampling; the operation being continued till only a small sample, sufficient for analysis, remains. If the substance to be sampled is a liquid, it should be thoroughly mixed and a sample quickly taken before any suspended matter settles.

(2) *Mechanical Division*.—Substances soluble in water, or readily soluble in acids, are only pulverized to a moderate degree of fineness; sufficiently fine, however, to insure an uniform sample. A porcelain mortar answers for this work. Substances not readily soluble in acids, or soluble only after fusion, must be reduced to an impalpable powder with an agate mortar.

(3) *Drying the Sample*.—The sample, when ready for analysis, must be in a definite state; that is, in a condition in which it can be obtained a second time, if by accident or otherwise a new sample must be prepared. This is accom-

plished by drying, which removes the hygroscopic moisture. The mode of drying will depend upon certain physical characteristics peculiar to different bodies.

*Classification With Reference to Mode of Drying.*

(a) Substances which lose water of constitution when exposed to air, are dried by pressing between folds of blotting-paper.

(b) Substances which only give off water in artificially dried air, are pressed between folds of blotting paper and then left for some time exposed to the air, protected from dust in some manner.

(c) Substances which undergo no change in dry air, but lose water at  $100^{\circ}$  C., are dried in a desiccator over fused  $\text{CaCl}_2$ , or strong  $\text{H}_2\text{SO}_4$ .

(d) Substances which give off all of their moisture at  $100^{\circ}$  C., but undergo no other change, are dried in a drying oven at  $100^{\circ}$  C.

(e) Some substances retain moisture at  $100^{\circ}$  C., but undergo no other change; this moisture is generally determined and reported in the analysis.

(f) A large number of substances, such as earths, rocks, minerals, etc., are always dried at  $100^{\circ}$  C., before analysis, and reports are made, based on such a drying.

(g) It should be remembered that a finely-powdered substance, when dried at  $100^{\circ}$  C., frequently absorbs moisture very rapidly when exposed to the air, especially on damp days, or in summer; and it is always advisable to weigh such substances as rapidly as possible and as soon as convenient after removal from the desiccator in which they have been cooled.

(4) *Calculations.*—Great care should be given to the calculation of results; which is a matter of vital importance in all cases, but especially where check analyses may be made by different chemists. Similar conditions should be observed as to *the atomic weights used, the temperature at which the substance is dried before weighing, and other points*:—such, for instance, as the iron value ascribed to the so-called “pure” iron wire used to standardize volumetric solutions for iron analysis, etc., etc., since many results disagree only through misinterpretation.

## GRAVIMETRIC DETERMINATIONS.

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The work under this head will consist of the quantitative analysis of certain substances, presented to the student in Boxes Nos. 1 to 6; the material in the boxes containing varying percentages of the substances to be determined. Reports should be returned upon each box, by number, showing clearly and neatly the weights obtained and the subsequent calculations used in obtaining the results.

A porcelain capsule (Meissen No. 6) will be used for weighings and ignitions. It should be cleaned, heated, cooled in the desiccator, and weighed before it is used in any case.

Great care should be used in determining the average weight of ash in the filters. Fold two or more filters, wrap with platinum wire and burn in the lamp to a white ash. Repeat the operation several times, and take the average weight for future use. Where "ashless" filters are used, this operation may generally be neglected. In burning the filters, the operation should be conducted over a piece of glazed paper, from which the ash may be conveniently removed to the capsule for weight.

To "filter by decantation," the beaker in which the precipitation has been made is set aside till the precipitate has subsided; the clear liquid above the precipitate is passed through the filter (which is then washed) and a sufficient excess of water (or whatever may be the washing solution) is added to the precipitate, which is again shaken up, or boiled if necessary, and allowed to subside as before;

after this, the supernatant liquid is again filtered, and the operation is continued until the precipitate is considered clean, finally throwing the residue on the filter, and giving it a final wash.

Care should be exercised by the student that his solutions do not, by addition of too great an amount of wash-waters or chemicals, attain too great a bulk for convenient use; at the same time, equal care should be taken that all residues on filters should be *thoroughly* washed, and that the solutions in use should not be too much condensed. A close following of the directions given will doubtless accustom the student to the use of proper quantities.

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#### Box No. 1.—Barium Chloride.

*Determination of Barium.*—Weigh very carefully about 0.500 grams of the substance; dissolve it in 100 cc. of distilled water, acidulate with HCl, boil and add, drop by drop, dilute H<sub>2</sub>SO<sub>4</sub> as long as a precipitate is formed. Boil for five minutes and set aside until the precipitate has completely subsided. Add carefully a drop or two of dilute H<sub>2</sub>SO<sub>4</sub> to make sure that all of the barium is precipitated. If this be the case, filter by decantation and wash with hot water until AgNO<sub>3</sub> produces no turbidity in the washings; being careful also that the upper edges of the filter are clean. Cover the funnel containing the filter and dry in the drying-oven; when dry, carefully remove most of the precipitate from the filter to a piece of glazed paper, place the filter and remaining contents in the capsule and ignite to a white ash; moisten the ash with a drop of dilute H<sub>2</sub>SO<sub>4</sub> and heat, very gently, until white fumes no longer arise; add the bulk of the precipitate from the glazed paper to that in the capsule, ignite

strongly, cool in the desiccator and weigh. From this weight subtract the weight of the filter-paper ash, if any; the remainder is the weight of barium sulphate. Make use of the atomic weights of the various elements involved to determine the per cent. of barium, as follows:—

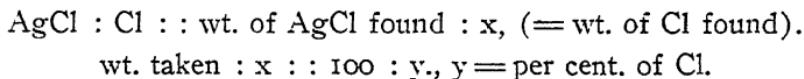


Wt. taken : x : : 100 : y., y = per cent. of Barium.

*Determination of Chlorine.*—Weigh carefully about 0.200 grams of the substance and dissolve in 50 cc. of warm, distilled water; add 20 cc. of silver nitrate solution, then acidify with dilute  $\text{HNO}_3$ , heat and agitate briskly; place the beaker containing the precipitate for a short time in a warm, dark place, then filter and wash with hot water until the filtrate shows no turbidity with HCl. Cover the funnel containing the filter and place in drying-oven till dry; remove the precipitate from the filter to a piece of glazed paper as completely as possible, place the filter in a weighed capsule and burn to ash; moisten the ash with a drop or two of  $\text{HNO}_3$  and heat gently, add a few drops of HCl and heat on the water-bath till dry. To the material in the capsule add the bulk of the precipitate from the glazed paper, and dry in the drying-oven. Cool the capsule and contents in the desiccator and weigh, reserving this weight as a check. Heat the capsule and contents with the lamp with the greatest care, until the precipitate *commences* to fuse at the edges; then cool in desiccator and weigh. If this precipitate be allowed to melt in the lamp, completely or in large part, the result will be too low and the operation worthless. Make use of the atomic weights involved to determine the per cent. of Cl, as below.

A far more convenient and accurate method than the pre-

ceding, consists in filtering the silver chloride upon a small, weighed, asbestos filter (such as is described in Part 2, under Rapid Analysis of Pig Iron) and, after thorough washing with hot water, using the filter-pump, washing once with alcohol and once with ether. The funnel and contents are then thoroughly dried at  $105^{\circ}$  C. and weighed after cooling in desiccator; the increased weight gives the weight of the silver chloride very accurately. The student should try both methods and compare results.



To remove the fused  $\text{AgCl}$  from the crucible, place upon it a piece of metallic zinc and add dilute sulphuric acid.

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### Box No. 2.—Magnesium Sulphate.

*Determination of Magnesium Oxide.*—Weigh carefully about 0.500 grams of the substance, dissolve in 25 cc. of distilled water (preferably in a small Erlenmeyer flask, for later convenience in agitation), add 15 cc. of  $\text{NH}_4\text{Cl}$  solution, then add 5 cc. of  $\text{NH}_4\text{OH}$ . If a precipitate is formed, it must be dissolved by addition of the least adequate quantity of  $\text{HCl}$ , and the solution again made alkaline with  $\text{NH}_4\text{OH}$ . The solution must be made cold; then add about 20 cc. of sodium-ammonium phosphate and agitate briskly; allow to stand till the supernatant liquid is clear (or, better, for ten hours) filter and wash well with a solution containing one part of  $\text{NH}_4\text{OH}$  and three parts of water, until the washings, acidified with  $\text{HNO}_3$ , show no turbidity on addition of  $\text{AgNO}_3$ . Cover the funnel containing precipitate and dry in drying-oven; ignite filter and precipitate in a weighed capsule, com-

mencing with a low heat and finishing with high heat, cool in desiccator and weigh. Repeat the ignition, cooling and weighing till constant weight is obtained. If, after ignition, the residue in the capsule is not pure white, moisten with  $\text{HNO}_3$  and again ignite, cool and weigh. By ignition the magnesium-ammonium phosphate precipitate is changed to magnesium pyro-phosphate. By use of the following calculation determine the per cent. of  $\text{MgO}$ .

$$\frac{\text{Mg}_2\text{P}_2\text{O}_7}{2 \text{ MgO}} = \frac{\text{wt. of Mg}_2\text{P}_2\text{O}_7 \text{ found}}{x}$$

$$\frac{\text{Wt. of substance taken}}{x} = \frac{100}{y} \cdot y = \text{per cent. of MgO.}$$

*Determination of Sulphuric Acid.*—Dissolve 0.500 grams in 30 cc. of distilled water, acidulate with  $\text{HCl}$ , boil and while boiling add slowly a boiling solution of  $\text{BaCl}_2$  as long as a precipitate is formed; boil five minutes and proceed from this point as directed in the determination of barium in Box No. 1. Calculate the per cent. of anhydrous sulphuric acid as follows:—

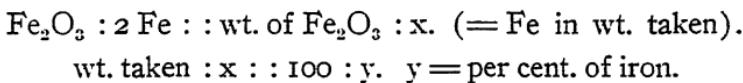
$$\frac{\text{BaSO}_4}{\text{SO}_3} = \frac{\text{wt. of BaSO}_4 \text{ found},}{x \text{ (= wt. of SO}_3 \text{ found,)}} \cdot \frac{\text{Wt. of substance taken}}{x} = \frac{100}{y}$$


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### Box No. 3.—Ferrous Sulphate.

*Determination of Metallic Iron.*—Weigh carefully 1 gram of the substance, and dissolve in a beaker in 25 cc. of distilled water strongly acidulated with  $\text{HCl}$ ; boil with occasional additions of small crystals of  $\text{KClO}_3$  until all of the iron is oxidized to a ferric condition. Continue the boiling, with further addition of  $\text{HCl}$  if necessary, until the  $\text{KClO}_3$  is

decomposed and the solution no longer emits an odor of chlorine. Add 75 cc. of distilled water and continue the boiling with the gradual addition of  $\text{NH}_4\text{OH}$  to slight excess. Boil again, allow the solution to subside, filter by decantation and wash thoroughly with hot water until a solution of silver nitrate produces no turbidity in the washings when acidulated with nitric acid. Cover the funnel containing the precipitate and dry in the drying-oven. Carefully remove the dried ferric hydrate from the filter, as completely as possible, to a piece of glazed paper, and ignite the filter, in a weighed capsule, till all carbonaceous matter is consumed to a white ash; add the remainder of the precipitate from the glazed paper to the capsule and ignite strongly, cool in the desiccator and weigh as ferric oxide. If the filter-paper is burned with the precipitate, the carbon gases reduce ferric to ferrous oxide, thus causing error. Determine the per cent. of metallic iron by the following calculation:—



*Determination of Sulphuric Acid.*—The operation is conducted as in the determination of iron, above, to the point where the iron is precipitated; at this point the iron is filtered at once (not by decantation) and the filtrate saved. Without washing, the precipitate is dissolved on the filter with HCl. and the filter is washed and discarded. Re-precipitate the iron as before; filter at once and wash; unite this filtrate with the reserved filtrate and precipitate the sulphuric acid with barium chloride; proceeding thereafter as under the determination of barium in Box No. 1. Make the calculations in the usual manner and report the per cent. of  $\text{SO}_4$ .

### Box No. 4.—Calcium Carbonate.

*Determination of Calcium Oxide.*—Take 0.200 grams of the substance, place it in a lipless No. 5 beaker, add 30 cc. of distilled water, cover with a cover-glass, gradually add HCl till effervescence ceases and heat till the substance is dissolved. Add NH<sub>4</sub>OH to alkaline reaction, and heat to boiling; while boiling add ammonium oxalate in slight excess, boil somewhat longer and allow the precipitate to settle for six hours in a warm place. The ammonium oxalate should be added drop by drop; thus insuring a more heavy precipitate. Filter by decantation, washing with hot water until the filtrate, acidulated with HNO<sub>3</sub>, gives no turbidity with silver nitrate solution. Cover the funnel as usual and dry in the drying-oven; ignite both paper and precipitate in the capsule, at a high heat, to the form of calcium oxide. To insure thorough conversion to this form, repeat the ignition, cooling and weighing till constant results are obtained. Calculate the per cent of calcium oxide as follows:—

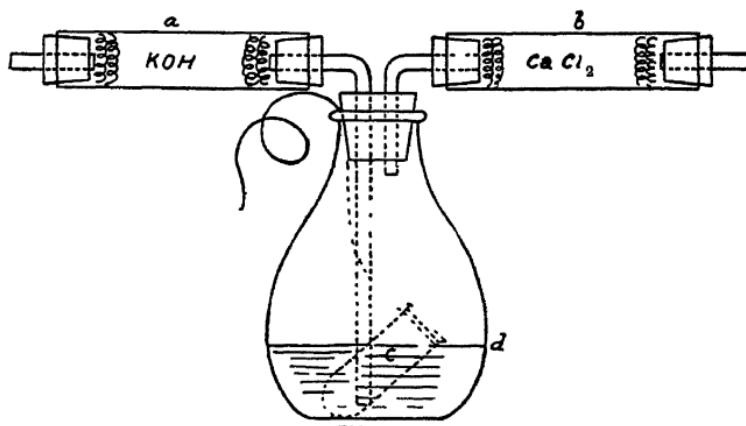
$$\text{CaCO}_3 : \text{CaO} :: \text{wt. of CaCO}_3 : x. \quad x = \text{CaO in wt. taken.}$$

$$\text{Wt. taken} : x :: 100 : y. \quad y = \text{per cent of CaO.}$$

*Determination of Carbon Dioxide.*—When carbonic acid is combined with a base it may be usually driven off by a strong acid and determined (a) by the loss of weight which the substance sustains, or (b) it may be dried in transit and received in a weighed solution of potash, in which case its weight is determined by the increased weight of the potash solution. Various forms of apparatus are sold by dealers for the determination of carbonic acid by the method (a) given above. The student may either use one of them (preferably Schroetter's apparatus) or make one for himself according to the sketch. A weighing-bottle or a small Erlen-

meyer flask may be used and fitted with a stopper through which pass two glass tubes, one connected with the drying-tube (*b*) containing granulated calcium chloride, the other connected with the tube (*a*) containing small pieces of potassium hydrate and passing nearly to the bottom of the flask. A small test-tube (*c*) is attached to a thin platinum wire which enters the flask beside the stopper. The flask is filled to the level (*d*) with HCl and the tube (*c*) is charged with a weighed portion of the substance and let down into the flask; not, however, dipping below the surface of the acid. Tube (*a*) is removed and the remaining apparatus weighed. Tube (*a*) is put on and air is aspirated from the end of tube (*b*); the tube (*c*) being gradually allowed to dip into the acid. After the substance in tube (*c*) is dissolved, air is drawn through tube (*b*) for a few minutes, tube (*a*) is again removed and the apparatus again weighed. The loss in weight is due to the carbonic acid liberated. The function of the tube (*a*) is to prevent access of carbonic acid from outside sources during aspiration. Calculate the per cent. of CO<sub>2</sub> as follows:—

$$\frac{\text{Wt. of substance in } (c)}{\text{Loss of wt. of apparatus}} = \frac{100}{x} \cdot x = \text{per cent. of CO}_2.$$



## VOLUMETRIC ANALYSIS.

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Volumetric analysis effects the quantitative determination of a body by converting it from a definite state to another equally definite state, by means of a fluid of accurately known power of action, and under circumstances which permit the analyst to mark with rigorous precision the exact point when the conversion is accomplished.\* The reagent and the material under examination must therefore be in solution.

The reagents, which must have in each case an exact and known strength, are called Standard Solutions, and are either Normal or Empirical.

*Normal Solutions* are used for determining the quantity of all metals with whose salts they produce distinct reactions. They are so prepared that one litre of such a solution, at a temperature of 16° C., shall contain an amount in grams of the active reagent equal to its molecular weight; regulated, however, by the number of basic hydrogen atoms in the acid from which the reagent may be derived. If the acid or salt constituting the active reagent is uni-valent, the full molecular weight is used; if it is bi-valent, one-half the molecular weight is used; if tri-valent, one-third is used. In certain cases, as will be seen later, this rule will not hold good, and such part of the molecular weight of the active reagent must be taken as its particular use may require. For convenience, normal solutions are frequently diluted to *deci-normal* or *centi-normal* strength ( $n/10$  and  $n/100$ ); these

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\*Fresenius.

solutions containing respectively one-tenth and one-hundredth the weight of the active reagent in the normal (N) solution.

*Empirical Solutions* are most frequently used in reactions upon salts for the determination of one metal only, and are generally of such strength that 1 cc. of the solution equals 1 per cent., or a fraction thereof, of the metal or salt to be determined, when titrating a solution containing a given weight of the material under examination.

*Example.*—By definition, a deci-normal (or n/10) solution of KOH will contain 5.6 grams of pure KOH per litre. In chemical practice the case might arise wherein it is desirable to examine a large number of samples of commercial citric acid, to determine the actual per cent. of acid therein. To avoid labor in calculating results it would then be advisable to use an empirical solution, which should be so composed that, if a one-gram sample be taken, in each analysis, of the material under examination, each cc. of the empirical solution used will represent one per cent. of citric acid. It will then be possible to weigh out one gram from each lot sent for analysis, dissolve each in a separate beaker, titrate each in its turn, and keep a record of the number of cc. of KOH solution consumed by each; this record will then represent directly the per cent. of citric acid contained in each sample. To make such an empirical solution, we proceed as follows:—If a one-gram sample of the citric acid is to be taken for analysis, one per cent. thereof would equal 0.010 grams; then each cc. of the KOH solution must equal 0.010 grams of pure citric acid, and we make the following equation, based on the respective molecular weights:—

$$\frac{\text{KOH (56.158)}}{\frac{1}{3} (\text{H}_3\text{C}_6\text{O}_7\text{H}_5 + \text{H}_2\text{O}) = 70.026} = \frac{x}{0.010} \cdot x = 0.0080195$$

From this we find that 0.0080195 grams of pure KOH will saturate 0.010 grams of pure citric acid; hence, each cc. of the KOH solution must contain 0.0080195 grams of KOH, which corresponds to 8.0195 grams per litre. It is, however, difficult to weigh an exact amount of KOH, since it absorbs moisture from the air; we are therefore obliged to reach this object indirectly, or by standardizing an unknown solution of KOH against some solution of an acid which can be accurately weighed. Such an one is oxalic acid  $H_2C_2O_4 + 2H_2O$ , whose molecular weight is 126.048, and whose hydrogen equivalent is 63.024. Then we have:

$$\frac{63.024 (\frac{1}{2} \text{ Oxalic})}{56.158 (\text{KOH})} = \frac{x}{8.0195} \cdot x = 8.9999$$

Hence, if we make a solution of oxalic acid containing 8.9999 grams per litre, and also make a KOH solution which will equal it, volume to volume, we will have in the latter the solution sought, or one containing, in each cc., 0.0080195 grams of pure KOH.

*Titrate* is a term applied to the method of comparing quantitatively the amount of pure substance contained in a given solution with the amount of another reacting substance contained in a standard or known solution. In other words, its meaning comprises the operations performed in so mixing the solutions used as to attain the end reaction.

*End Reaction* is the term applied to that point in the operation where no further change takes place between the known and the unknown. The end reaction must be manifest to the eye, either by some change in the solution itself, or by the use of an indicator. Reagents which produce no visible change cannot be used as standard solutions.

*Normal Factor* is a term used to express the amount in grams of the active reagent in 1 cc. of a normal solution.

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### THREE METHODS IN VOLUMETRIC ANALYSIS.

The operations in volumetric analysis are conveniently considered under three heads, dependent upon the object of the analysis and the character of the reactions employed; the methods are as follows:—

- (1) Saturation, or Acidimetry and Alkalimetry.
- (2) Oxidation and Reduction.
- (3) Precipitation.

#### (1.) ACIDIMETRY AND ALKALIMETRY.

This method has for its object the determination of the quantity of actual acid or alkali in a given solid or liquid. In titrating an acid against an alkali, the point of exact saturation or neutralization must necessarily be made evident in some manner; this is accomplished by the use of an indicator, which usually records the neutral point by a change of color.

In the following work (unless otherwise suggested) the indicator used is *phenol-phthalein*, which is a yellowish powder, soluble in alcohol. To prepare a solution for use, dissolve about 0.010 grams in 10 cc. of 50% alcohol. One or two drops are sufficient for each titration. Acids produce no change in color, but alkalies produce an intense purple-red. This, though perhaps not the best indicator (see Indicators, in Appendix), has been found to work well in the hands of beginners, on account of its great sensitiveness. It cannot be used in titrating ammonia, or the caustic alkalies when ammoniacal salts are present. Cold or only moder-

ately warm solutions must be used in titrating oxalic, citric, tartaric, acetic and other organic acids with KOH and NaOH. Hot solutions must be used in titrating alkaline or earthy hydrates, carbonates, bi-carbonates and sulphides with mineral acids.

### Preparation of Standard Solutions.

It has been before suggested that it is not always possible to obtain the reagent of which we wish to make a standard solution in a definite, permanent and weighable form, so that the exact amount necessary for any desired standard solution—either normal or empirical—can be weighed, for subsequent solution and dilution to the necessary volume. In such cases, a solution of unknown strength is made of the reagent, and this solution is standardized by titration with some standard solution; then, by calculation, the unknown solution is diluted to the necessary strength.

It is the intention that the student shall prepare the following solutions, in order, and reserve them for use in the analysis of the volumetric unknowns which will be given him. Equal volumes of all standard solutions of a given class—such as deci-normal—must exactly neutralize each other; provided, of course, that one be acid and the other alkaline. Thus, one cc. of any deci-normal or n/10 acid will exactly neutralize a solution (of any size) which is rendered alkaline by one cc. of any deci-normal or n/10 alkali. In preparing n/10 solutions for this part of the work, the first one will be of oxalic acid, since this acid can be obtained in definite and weighable form. The strictest care and method is advised in the preparation of these solutions, since, without it, all of the following analyses will be of doubtful value;

their value being altogether a function of the correctness of the standard solutions.

#### N/10 Oxalic Acid Solution.

By previous definition, this solution should contain, in one litre, a number of grams of pure oxalic acid equal to one-tenth the molecular weight of oxalic acid, divided by the number of atoms of basic hydrogen which the acid contains. Crystallized oxalic acid has the formula:  $H_2C_2O_4 + 2H_2O$ , and its molecular weight is therefore 126.048. Hence, we have:  $1/10$ th of 126.048  $\div 2 = 6.3024$ .

Weigh out *exactly* 6.3024 grams of freshly prepared, clean crystals of oxalic acid, dissolve in distilled water and dilute *exactly* to one litre. Each cc. of this solution should contain 0.0063024 grams of oxalic acid; therefore the n/10 factor is 0.0063024.

#### N/10 Potassium Hydrate Solution.

Take 50 cc. of the table reagent and dilute with distilled water to 600 cc.; cool and titrate with n/10 oxalic acid as follows:

Take 5 cc. of the unknown KOH solution, in a No. 1 beaker, place it on a piece of white paper and underneath the burette containing standard n/10 oxalic acid; add two drops of the indicator and mix with a small glass stirring-rod. Run into it from the burette, drop by drop and with care, the standard oxalic acid, stirring the mixture after each addition, until a drop of the acid just disperses the red color. Make a note of the number of cc. of n/10 oxalic required. Repeat this operation and record the result. Make two similar titrations, but using 10 cc. of the KOH solution; also

two others, using 15 cc. of the KOH solution. If there be no wide divergence, take the average of the six titrations for a result.

To calculate the necessary dilution of the KOH solution: suppose the average result showed that 5 cc. of the KOH solution required 8 cc. of the n/10 oxalic to produce the end reaction; the KOH solution is therefore too strong, and must be diluted with water, in order to make it deci-normal like the oxalic solution. Suppose that there are 550 cc. of the KOH solution left in the graduated cylinder; how many cc. of a deci-normal solution will it make?

$$5 \text{ cc.} : 8 \text{ cc.} :: 550 \text{ cc.} : x. \quad x = 880 \text{ cc.}$$

Therefore, add to the KOH solution in the cylinder distilled water to bring the volume of solution up to 875 cc., mix thoroughly and again titrate with n/10 oxalic acid; making three titrations, and using 25 cc. each time. Make the necessary calculations and, if the final result confirms the first one, take the present reading of the KOH solution in the cylinder and dilute it with the necessary amount of distilled water. The molecular weight of KOH being 56.158 and its hydrogen equivalent being one, a deci-normal solution should contain 5.6158 grams per litre, and the n/10 factor is 0.0056158.

#### N/10 Sulphuric Acid Solution.

Take 5 cc. of the table reagent, dilute to 300 cc. with distilled water *in a porcelain dish*, allow to cool thoroughly, and transfer to the graduated cylinder. Titrate as before, using standard n/10 KOH, but do not use a glass-stoppered burette; such are injured by holding strong alkalies. Make the calculation for dilution of the acid as before. The molecular

weight of sulphuric acid being 98.076, with two atoms of basic hydrogen, we have  $98.076 \div 2 \times 1/10 = 4.9038$ ; consequently, the deci-normal factor is 0.0049038.

#### *N/10 Nitric Acid Solution.*

Take about 5 cc. of the table reagent, which should be free from nitrous fumes, dilute with 300 cc. of distilled water, and titrate with n/10 KOH; following the directions given for sulphuric acid. The molecular weight of nitric acid is 63.048 with one atom of basic hydrogen; consequently, its deci-normal factor is 0.0063048.

#### *Normal Oxalic Acid Solution.*

Weigh carefully 15.756 grams of clean crystals, dissolve in 150 cc. of distilled water and dilute to 250 cc.

#### *Normal Sodium Hydrate Solution.*

Take about 15 grams of sodium hydrate, dissolve it in 150 cc. of distilled water in a porcelain dish, cool, transfer to a graduated cylinder and standardize by titration with normal oxalic acid.

#### *Normal Tartaric Acid Solution.*

Take about 20 grams of tartaric acid, dissolve in 150 cc. of distilled water, filter if necessary, cool and titrate with normal NaOH.

#### **Examples for Practice.**

The student will titrate each of the following table reagents against one of the prepared standard solutions, for the purpose of determining the per cent. of acid or alkali.

$\text{HNO}_3$ , n/10 factor = 0.0063048     $\text{HC}_2\text{H}_3\text{O}_2$ , n/10 factor = 0.0060032  
 $\text{HCl}$ , n/10 factor = 0.0036458     $\text{KOH}$ , n/10 factor = 0.0056158

Before proceeding with these operations, attention is called to the following remark and to the method used in determination of the percentage composition of HCl, as given below; also, to the fact that the titration of acetic acid by a standard alkali is not rigidly exact, since neutral acetates have an alkaline reaction. Volatile liquids, such as  $\text{NH}_4\text{OH}$  must be weighed in well stoppered bottles.

*Remark Concerning Weighing.*—All material, whether solid or liquid, which is to be titrated for the per cent. of any ingredient, must be weighed. An ordinary  $1\frac{1}{2} \times 3$ -inch weighing tube may be used or the student may use a 2-ounce Florence flask, which should be cleaned, dried and graduated, by filling the bulb and a portion of the neck from a burette, and placing a mark at the meniscus, which indicates a convenient, even number of cc. used.

*Example. Titration of HCl.*—Take about 5 cc. of the table reagent, place it in the weighing flask and weigh; dilute with water. Mix thoroughly, cool and dilute to the mark. Fill a glass-tap burette with this solution, and a Mohr's burette with the KOH solution, (n/10). Run into a small beaker 10 cc. of the HCl solution, add two drops of the indicator and titrate with the n/10 KOH; repeat the titration three or four times and take the average result.

*Calculation for Per Cent. of HCl.*—Of the table reagent 5 cc. were taken, which weighed 5.6 grams. The weighing flask holds 60 cc., and the 5 cc. weighed were diluted to that mark.

Upon titration it took 40 cc. of n/10 KOH to neutralize 10 cc. of the diluted HCl, then

$$10:40::60 \text{ (No. of cc. of diluted HCl)} : x,$$

$x = 240$  cc. of n/10 KOH. From this proportion it is evident that the 5.6 grams of HCl taken, which were diluted to 60 cc. are equivalent to 240 cc. of n/10 KOH; consequently, in 5.6 grams of acid taken, there is enough active reagent to make 240 cc. of n/10 HCl.

Now in each cc. of n/10 HCl there are 0.0036458 grams of HCl, since the molecular weight of HCl is 36.458; then, in 240 cc. of n/10 HCl there are  $240 \times 0.0036458 = 0.874992$  grams of HCl.

To find what per cent. this amount is of the weight taken (5.6 grams), we have

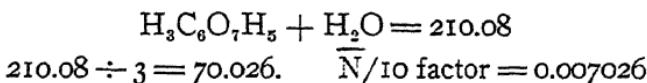
$$5.6 : 0.874992 :: 100 : y. \quad y = 15.62\% \text{ of HCl.}$$


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### Volumetric Examination of Five Acids or Alkalies.

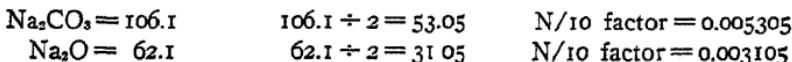
The student will determine the per cent. of the ingredient sought in each of the following substances, by volumetric analysis; following the methods before given, and making reports of the results found, with neat records of the weights and calculations used.

#### Box No. 1.—Citric Acid.



Weigh carefully about 0.200 grams of the substance, in the weighing-flask, dissolve in distilled water, dilute to the mark and titrate with n/10 KOH.

#### Box No. 2.—Sodium Carbonate.



Report the per cent. of  $\text{Na}_2\text{CO}_3$  and also of  $\text{Na}_2\text{O}$ .

Weigh carefully about 0.500 grams in the weighing-flask, dissolve in distilled water and dilute to the mark. Measure carefully 10 cc. of this solution, by means of a pipette, place it in a small flask, add some distilled water and two drops of the indicator; now run into the flask, from a burette, deci-normal  $\text{H}_2\text{SO}_4$ , one-half cc. at a time, boiling after each addition, until the n/10  $\text{H}_2\text{SO}_4$  is in excess of the amount required for neutralization; recording accurately the number of cc. of n/10  $\text{H}_2\text{SO}_4$  so used. Boil at least five minutes and titrate back the excess of  $\text{H}_2\text{SO}_4$  with deci-normal KOH. An additional drop or two of the indicator may be required from time to time during the titration. The difference between the amount of n/10  $\text{H}_2\text{SO}_4$  and the n/10 KOH used is the amount of n/10 acid necessary to neutralize the alkali in the sample taken. By use of the deci-normal factors and the weight of substance taken, determine and report the percentages of the ingredients sought.

#### **Box No. 3.—Sodium Bi-Carbonate.**

$$\text{NaOH} = 40.058 \quad \text{N/10 factor} = 0.0040058$$

Follow closely the directions given under the examination of the substance in Box No. 2, and report the per cent. of sodium hydrate.

#### **Box No. 4.—Calcium Carbonate.**

$$\begin{array}{lll} \text{CaO} = 56.1 & 56.1 \div 2 = 28.05 & \text{Normal factor} = 0.02805 \\ \text{CO}_2 = 44. & 44 \div 2 = 22. & \text{Normal factor} = 0.022 \end{array}$$

Weigh carefully about 0.050 grams, place it in a large beaker, add sufficient distilled water to cover the bottom of the beaker, then titrate with normal  $\text{HNO}_3$ , instead of

$\text{H}_2\text{SO}_4$ , according to the directions given for Box No. 2. Report the per cent. of  $\text{CO}_2$ , and the corresponding per cent. of  $\text{CaO}$ .

**Bottle No. 5.—Caustic Potash and Soda Solution.**

Normal factor for  $\text{KOH} = 0.056158$ .

Normal factor for  $\text{NaOH} = 0.040058$ .

For adaptability to the following method, the above solution must be at least of normal strength. Weigh carefully about 10 grams of the mixed alkalies in a small, weighed, Erlenmeyer flask. Do not dilute with water. From a burette carefully add normal tartaric acid till the solution is neutral or faintly acid; note the exact amount of tartaric acid used and run in just as much more. Cork the flask and shake violently for a few minutes, when the potassium bi-tartrate will almost completely separate, it being insoluble in sodium bi-tartrate. Filter; when the filtrate has all passed through, rinse out the flask with *not over* 5 cc. of distilled water and pour it on the filter. When all has passed through, titrate the filtrate with normal  $\text{NaOH}$ ; the number of cc. of normal  $\text{NaOH}$  used equals the amount of soda in the mixture.

*Calculation.*—If 10 grams of the mixed alkalies were taken, and if a total of 24 cc. of normal tartaric acid were used (forming bi-tartrate of both sodium and potassium), this indicates that there is a total of 12 cc. of normal alkali in the mixture. In the final titration with normal  $\text{NaOH}$ , if 5 cc. of the normal  $\text{NaOH}$  were used (for titrating the tartaric acid uncombined with potassium) we have: 12 — 5 = 7; which is the number of cc. of normal  $\text{KOH}$  in the mixture. Thus we have:  $5 \times 0.040058 = 0.20029$  grams of

$\text{NaOH}$ , and  $7 \times 0.056158 = 0.393106$  grams of  $\text{KOH}$  in the ten grams of the solution taken. Calculate and report the per cent. of each alkali.

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#### (2). OXIDATION AND REDUCTION.

This method of volumetric analysis is probably more generally adapted for use than any other, and many of its applied uses are of extreme accuracy. As it is evident that the accuracy of the results obtained is, with careful manipulation, purely a function of the rectitude of the standard solutions used, *the greatest care* must be exercised in standardizing them and also in selecting, whenever possible, methods employing standard solutions of the more stable salts, such as  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{As}_2\text{O}_3$ . As oxidizing agents  $\text{K}_2\text{Cr}_2\text{O}_7$ , I, and  $\text{KMnO}_4$  are more generally used, with  $\text{As}_2\text{O}_3$ ,  $\text{H}_2\text{C}_2\text{O}_4$ ,  $\text{Na}_2\text{S}_2\text{O}_3$ ,  $\text{FeSO}_4$  and  $\text{SnCl}_2$ , as reducing agents.

The student will prepare the various volumetric standard solutions described below and, by their use, make the determinations required in the various substances contained in the boxes and bottles, numbered six to eleven, which follow; reporting results and calculations as before.

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#### *N/10 Potassium Permanganate.*

$$\text{KMnO}_4 = 158.15 \quad 158.15 \div 5 = 31.63 \\ \text{n/10 factor} = 0.003163$$

Select some clean crystals, dry them for forty-eight hours in a desiccator containing  $\text{H}_2\text{SO}_4$ , then weigh very carefully 3.163 grams, dissolve in distilled water and dilute carefully to one litre. If the salt is pure, the solution will be deci-

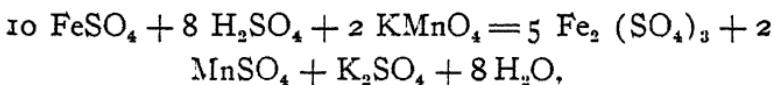
normal; but, as this is not always the case, the solution must be titrated against some reducing agent which has a definite and constant composition. Standard  $\text{KMnO}_4$  cannot be used in titrating solutions in which there is much free HCl, since free HCl reduces  $\text{KMnO}_4$ .

Three methods of titrating the n/10 permanganate are now given, for the purpose of establishing its correctness; (a) with pure iron, (b) with n 10 oxalic acid, and (c) with n/10 sodium thio-sulphate. Of these substances, the iron solution is always prepared for immediate use, the n/10 oxalic acid is already on hand, and the n/10 thio-sulphate will shortly be prepared, when it may be used.

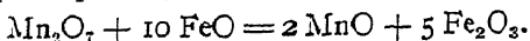
#### *Titration of Permanganate.*

(a) *With Iron Wire.*—Prepare several 100 cc. flasks, with stoppers, through each of which is passed a small glass tube, about 12 inches in length and drawn down to a small opening at its upper end; to serve the purpose of condensing fumes and causing their return to the flask. The tubes may be of one-quarter inch diameter, or less. Weigh carefully several portions of pure iron wire of about 0.100 grams each (whose absolute iron contents should be previously established) and digest one portion in each flask, on the water-bath, in dilute  $\text{H}_2\text{SO}_4$ . When all of the iron is dissolved, rinse the condensing tube into its flask and titrate at once with the  $\text{KMnO}_4$  solution, till a faint, permanent pink color is obtained. Compare the results obtained and, if there be no wide divergence, retain the average result.

The reaction is as follows:—



or, considering only the active reagents and thereby obtaining a simpler equation, we have:



The calculation of results may be made as follows:—The atomic weight of iron is 55.9 and its n/10 factor is 0.00559; hence, if one of the flasks contained 0.100 grams of iron wire, which has been previously found to contain 98.38 % of pure iron, we have:  $0.09838 \div 0.00595 = 17.6$ ; which equals the number of cc. of the  $\text{KMnO}_4$  solution which should have been used in titrating 0.09838 grams of iron, *if the  $\text{KMnO}_4$  solution was deci-normal*. We may find the  $\text{KMnO}_4$  solution either too weak or too strong; if it be too weak, add a *solution* of stronger  $\text{KMnO}_4$ , mix thoroughly and titrate again; if, however, the average result of the several titrations shows the  $\text{KMnO}_4$  solution to be too strong, figure the necessary dilution as follows:—

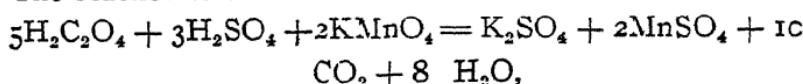
Suppose that the 0.09838 grams of pure iron took only 16.6 cc. of the  $\text{KMnO}_4$  solution, instead of 17.6 cc.; then  $17.6 \div 16.6 = 1.06$ , which is the factor by which the volume of  $\text{KMnO}_4$  solution in the cylinder must be multiplied in order to be deci-normal. If then, the above factor 1.06 be the average found in the several titrations, multiply the number of cc. of the  $\text{KMnO}_4$  solution in the graduated cylinder by 1.06, and carefully dilute the solution to the required volume with distilled water. Mix thoroughly and titrate with other portions of iron wire, until the solution is found to be deci-normal.

If there should be difficulty in establishing the exact iron content of the wire, pure iron may be obtained by electrolysis, as follows:—Dissolve from 6 to 8 grams of ammonium oxalate in the least quantity of water; gradually add to this solution, with constant stirring, a solution in water of about

7 grams of ammonio-ferrous-sulphate (which is equivalent to about 1 gram of iron) and dilute with water to 100 or 150 cc. The solution is placed in a clean platinum dish, the positive electrode is completely immersed in the liquid, and a current of from 1 to 1.5 amperes is passed through the solution for from 2 to 4 hours. At this time, or when sufficient iron is precipitated, remove the electrode, pour the solution from the dish, wash the latter three times with cold water and once with alcohol, dry in the air-bath and desiccator and weigh. The iron should be pure, and may be dissolved from the dish in dilute  $H_2SO_4$ , with addition of a little  $Na_2CO_3$  to prevent oxidation of the iron. A little strong  $H_2SO_4$  is added and, when solution is complete, the iron is titrated at once with the solution of permanganate. The exact weight of the iron titrated is found by cleaning and drying the platinum dish, and subtracting its weight from the weight last obtained.

(b) *With N/10 Oxalic Acid.*—Measure 10 cc. of the deci-normal oxalic acid into a small beaker, by means of a burette; add a few drops of dilute  $H_2SO_4$  (1 to 5), warm to 60° C. and titrate with the  $KMnO_4$  solution to a faint, permanent rose color. Repeat the titration upon a like quantity of the n/10 oxalic acid; then make similar titrations using 15 cc. of the n/10 oxalic acid. If there be no particular divergence, take the average of these results.

Especial care should be exercised in these titrations, since the reaction is less decisive than in the titration with iron. The reaction is as follows:—



or, more simply,  $Mn_2O_7 + 5C_2O_4 = 10CO_2 + 2MnO$ .

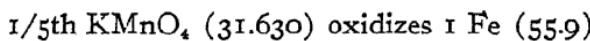
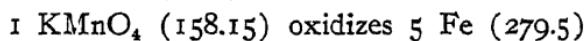
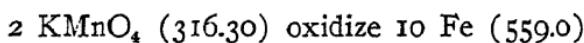
(c) *With N/10 Sodium Thio-Sulphate.*—Place in a flask

about 30 cc. of table reagent KI which has no free iodine; add two cc. of HCl of specific gravity 1.12, dilute largely with distilled water, and run in 5 cc. of the  $\text{KMnO}_4$  solution; cork the flask and shake thoroughly, keeping the solution cold. Now, titrate back with n/10 sodium thio-sulphate until the solution is colorless, then run in the  $\text{KMnO}_4$  solution, drop by drop, till the iodine color reappears. Repeat this operation, using a larger quantity of the  $\text{KMnO}_4$  solution, till the results are satisfactory.

#### *Discussion.*

In the equations representing the reactions between  $\text{KMnO}_4$  and (1)  $\text{FeSO}_4$  and (2)  $\text{H}_2\text{C}_2\text{O}_4$  we notice that, in each case, *two* parts of  $\text{Mn}^{\text{VII}}$  (manganese with seven bonds) oxidize *ten* parts of the metals acted upon; in one case ten parts of  $\text{Fe}^{\text{II}}$  (ferrous iron) are oxidized to  $\text{Fe}^{\text{III}}$  (ferric iron), and in the other case ten parts of  $\text{C}^{\text{III}}$  are oxidized to  $\text{C}^{\text{IV}}$ ; or, to reduce, *one* part of  $\text{KMnO}_4$  oxidizes *five* parts of each metal.

Consider the case of the reaction with iron; and, to make deci-normal  $\text{KMnO}_4$  upon the basis of this reaction, we have the following reasoning:—Since one part of  $\text{KMnO}_4$  (molecular weight = 158.15) causes an exact and distinct reaction with five parts of iron (atomic weight = 55.9), a solution of  $\text{KMnO}_4$  will be normal *as regards iron* if its strength, as based upon its molecular weight, be made one-fifth; that is to say,



or, 31.630 grams of  $\text{KMnO}_4$  diluted to one litre, form a

normal solution, since this weight produces an exact and distinct reaction with 55.9 grams of metallic iron. Therefore, the amount of permanganate necessary for a deci-normal solution will be one-tenth of the above weight, or 3.163 grams.\*

Now, later, we shall make use of the reaction between  $\text{KMnO}_4$  and  $\text{MnSO}_4$  for the purpose of making a volumetric determination of manganese. The reaction between the two salts is as follows:— $\text{Mn}_2\text{O}_7 + 3\text{MnO} = 5\text{ MnO}_2$ , or, two parts of  $\text{Mn}^{\text{vii}}$  oxidize three parts of  $\text{Mn}^{\text{ii}}$ ; or, 2  $\text{KMnO}_4$  (316.3) oxidize 3  $\text{Mn}$  (165). Now, the atomic weight of manganese is 55; and, if we were to make a solution of n/10  $\text{KMnO}_4$  by similar reasoning to that used in the reaction with iron, each cc. of the n/10  $\text{KMnO}_4$  solution should be made to equal 0.0055 grams of manganese, and would therefore, by the equation given above, contain 0.010543 grams of  $\text{KMnO}_4$ . This, however, is not made use of, for the so-called deci-normal  $\text{KMnO}_4$  is deci-normal *with respect to iron*, and not with respect to manganese; and the so-called deci-normal factor for manganese is 0.00165, instead of being 0.0055 as it otherwise would be.

In general, then, *always write the equation for the reaction between the substances to be titrated.* This will remove the ambiguity which may surround the subject for the beginner, and which is rarely removed by an adequate explanation.

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\*The iron is considered as *metallic* (instead of using the ferrous sulphate—as it occurs in the solution—and *its* molecular weight), since the student will more readily recognize the atomic weight of iron (55.9) as being the weight which, if dissolved and diluted to one litre, will, by previous definition, make a normal solution. A very slight consideration will make it evident that the molecular weight of ferrous sulphate would answer the same purpose in the calculation.

*N/10 Potassium Bi-Chromate.*

$$\text{K}_2\text{Cr}_2\text{O}_7 = 294.5 \quad 294.5 \div 6 = 49.083.$$

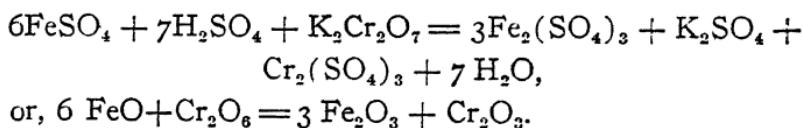
Weigh carefully 4.9083 grams of the pure salt, dissolve in distilled water and dilute to one litre.

Potassium bichromate possesses the advantage over permanganate that it is permanent in solution, may be easily obtained in a pure state, and may be used in the presence of free sulphuric or hydrochloric acid. It possesses a disadvantage, in that it generally requires an external indicator, and cannot well be used in the presence of zinc salts when the indicator used for iron (described below) is used.

The indicator referred to is potassium ferri-cyanide, which must be freshly prepared, by dissolving a minute fragment in distilled water, and which must be so dilute that a drop, placed upon a white surface, shows but a very faint yellow color.

*Titration of Bi-Chromate.*

(a) *With Iron Wire.* Dissolve several samples of the iron wire in the same manner used in (a) under titration of permanganate. In titrating a sample with the bi-chromate, wash the flask and its contents into a beaker, dilute *largely* with distilled water and titrate *without delay*, testing the condition of the solution in the beaker after each addition of bi-chromate, by bringing a drop in contact with a drop of the indicator placed on a porcelain slab. When the oxidation of the iron solution is complete, contact with the indicator will give no blue color after standing two minutes. The reason for dispatch in this operation lies in the fact that the ferrous solution is apt to oxidize with undue standing, thus destroying the accuracy of the determination. The reaction is as follows:—



(b) *With N/10 Sodium Thio-Sulphate.*—Titrate in the same manner as in (c) under titration of permanganate.

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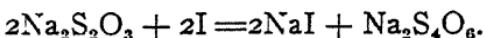
### *N/10 Iodine.*

Iodine = 126.85      12.685 grams per litre.

Place about three grams in a glass-stoppered weighing-bottle and weigh. Iodine is very volatile, and the bottle must be kept closed while weighing. Prepare a solution of potassium iodide, by taking ten grams and dissolving it in 100 cc. of distilled water; transfer the iodine to the graduated cylinder, carefully rinsing out the weighing-bottle with the solution of potassium iodide, and shake the cylinder till the iodine is dissolved. This solution may take some time, and great care must be taken that no particles of undissolved iodine remain. A solution of iodine changes after standing some time; consequently, the standard solution should always be tested before using.

### *Titration of Iodine.*

(a) *With N/10 Thio-Sulphate.*—Measure carefully from a burette 10 cc. of the n/10 sodium thio-sulphate, add a few drops of starch indicator (Reagent 22.) and carefully titrate with the iodine solution till the addition of one drop produces a permanent blue color. The solution must not be heated. The reaction is as follows:—



(b) *With N/10 Arsenious Acid.*—Measure carefully from a burette 10 cc. of n/10 arsenious acid (see next solu-

tion below) add a few drops of starch indicator and titrate as in the case of sodium thio-sulphate. The reaction is as follows:— $\text{As}_2\text{O}_3 + 2\text{Na}_2\text{O} + 4\text{I} = \text{As}_2\text{O}_5 + 4\text{NaI}$ .

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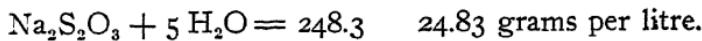
#### *N/10 Arsenious Anhydride.*



Weigh approximately three grams, place it in a flask, add 25 grams of pure sodium bi-carbonate and about 250 cc. of distilled water; boil till dissolved, cool, decant or filter the clear solution into a graduated cylinder; titrate with n/10 iodine, using starch indicator, and calculate the dilution required to make the solution deci-normal. After diluting with distilled water to the necessary volume, titrate again to make certain of its accuracy.

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#### *N/10 Sodium Thio-Sulphate.*



Powder a quantity of the pure salt, and dry by pressing it between folds of blotting paper. Weigh exactly 24.83 grams, dissolve in distilled water and dilute to one litre. The solution should be kept in a dark place, as it is somewhat unstable. It should always be examined before using.

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**NOTE.** Standard solutions of ferrous sulphate and ferrous-ammonium-sulphate ( $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 + 6\text{H}_2\text{O}$ ) are frequently used; but, as they are liable to suffer oxidation of their iron, and consequent deterioration, it is held to be better, in all cases, to prepare fresh solutions of metallic iron as standards, if iron wire can be obtained whose actual iron content is known. Directions for preparing such solutions of ferrous sulphate are given under (a) in the titration of permanganate.

**Box No. 6.—Oxide of Iron.**

Determine the per cent. of iron by titration with n/10 permanganate, as follows:—Dry a sample of the substance in the drying-oven at 100° C. and cool in the desiccator. Weigh carefully about 0.500 grams, place it in a No. 3 lipless beaker, add strong HCl to fill the beaker about one-third of an inch, cover with a cover-glass and heat on the water-bath till solution is complete; cool, then add 2 cc. of strong H<sub>2</sub>SO<sub>4</sub> and evaporate till SO<sub>2</sub> fumes appear; cool, and dilute with distilled water to a given volume. Of this solution, measure carefully 20 cc. into a beaker, dilute with distilled water, add a few scraps of metallic zinc and enough H<sub>2</sub>SO<sub>4</sub> to produce a brisk evolution of hydrogen; heat on the water-bath until all of the iron is reduced to the ferrous condition; remove the zinc and heat till all bubbles are removed, then titrate with n/10 KMnO<sub>4</sub>.

The zinc used should always be tested, to determine its reducing power upon KMnO<sub>4</sub>; this will supply a correction factor for the amount of KMnO<sub>4</sub> used in the iron titration.

After using the above method, refer to Method No. 2, under Iron Ores, in Part 2, of this book..

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**Box No. 7.—Iron Ore.**

Determine the per cent. of metallic iron by titration with n/10 sodium thio-sulphate, as follows:—Pulverize about one gram of the substance very finely in an agate mortar, dry at 100° C., accurately weigh about 0.500 grams and dissolve in strong HCl, in the same manner as that given for Box No. 6. When dissolved, cool, transfer to a graduated flask, dilute with distilled water to 200 cc.; carefully measure out

50 cc. of this solution, place in a beaker, dilute largely with distilled water, add 3 cc. of a 1% solution of copper sulphate and two drops of KCyS solution, and titrate with n/10 sodium hyposulphite until the red color disappears; make record of this operation, then add a few drops of starch indicator (Reagent 22.) and titrate with n/10 iodine till the blue color appears: thus checking the thio-sulphate titration. During the titration with thio-sulphate the solution must be cold and must remain clear.

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#### Box No. 8.—Ferrous and Ferric Oxides.

Determine the per cent. of ferrous oxide (n/10 factor, 0.00719) and the per cent. of ferric oxide (n/10 factor, 0.00799) in the following manner:—

Pulverize a portion of the sample very finely in an agate mortar, dry at 100° C., carefully weigh about 0.500 grams and dissolve in strong HCl on the water-bath; using a flask provided with a condensing-tube, such as was used in the solution of iron wire. Pour the solution and the rinsings of the flask into a No. 4 beaker, dilute largely with distilled water, and titrate without delay with n/10  $K_2Cr_2O_7$ , as before directed. Properly calculated, the result will give the per cent. of iron occurring in the sample as *ferrous oxide*.

Take another sample of about 0.500 grams, prepared in the same manner, place it in a No. 0 lipless beaker, add 15 to 25 cc. of strong HCl, cover with a cover-glass and heat on the water-bath till dissolved. Wash the cover-glass into the solution and, without cooling, add very carefully, drop by drop, a solution of  $SnCl_2$  (Reagent 4.), agitating gently with a rod after each addition, until the solution becomes colorless; thus indicating the complete reduction of the iron to the

ferrous condition. Wash the contents of the beaker into a No. 5 beaker, dilute with 300 cc. of distilled water, add 30 cc. of a solution of  $HgCl_2$  (Reagent 5.) and titrate with n/10  $K_2Cr_2O_7$  as before directed. The last result will give the total amount of iron in the sample. Calculate the ferrous iron found in the first operation in terms of ferric oxide, and subtract it from the last result; this remainder will represent the amount of ferric iron in the sample.

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**Box No. 9.—Arsenious Anhydride.**

$As_2O_3 = 198$ . N/10 factor for  $As_2O_3 = 0.00495$ ,  
for As = 0.00375.

Dry the sample at  $100^{\circ} C.$ , cool, weigh carefully about 0.200 grams and dissolve it in 50 cc. of a saturated solution of pure  $NaHCO_3$  with the aid of heat; cool and dilute to a given volume; measure out 25 cc. and titrate with n/10 iodine, according to directions previously given.

This method will serve for  $As_2O_3$ , but not for the  $As_2O_5$  which is always present in the commercial article. If the  $As_2O_5$  is to be determined, it may be reduced to  $As_2O_3$  by the use of a strong solution of  $H_2SO_3$ . (See Sutton's Volumetric Analysis, 6th Edition, page 137.)

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**Bottle No. 10.—Tincture of Iodine.**

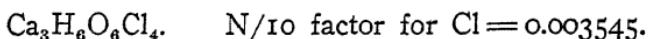
Iodine = 126.85. N/10 factor = 0.012685.

First test the sample to see whether it is a simple or compound tincture, by adding distilled water to a small portion; water will produce a precipitate in the former, but not in the latter. If it is a simple tincture, dry the weighing-flask,

put in 10 cc. of the tincture and weigh; add 25 cc. of solution of potassium iodide and dilute to the mark. If it is a compound tincture, weigh as above and dilute to the mark without the addition of potassium iodide. Thoroughly mix the solution in the flask, accurately measure portions of 25 cc. and titrate with n/10  $\text{As}_2\text{O}_3$  and also with n/10  $\text{Na}_2\text{S}_2\text{O}_8$ , according to directions before given.

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### Bottle No. 11.—Bleaching Powder.



Commercial bleaching powder consists of a mixture of calcium hypo-chlorite (the true bleaching agent), calcium chloride and hydrate and, in some cases, calcium chlorate. It is generally valued and sold in this country by its percentage of chlorine, of which it contains a maximum of about 39 per cent. Carefully weigh about five grams in a well-stoppered weighing-flask, place in a porcelain mortar and triturate with distilled water; pour the milky liquid into a graduated cylinder, triturate the residue with water, and repeat the operation till all the material has been transferred to the cylinder. Dilute with distilled water to 500 cc., shake well and measure out 25 cc. for titration. Measure into it from a burette an excess of n/10  $\text{As}_2\text{O}_3$  (about 40 cc.), mix thoroughly, add starch indicator and titrate back the excess of n/10  $\text{As}_2\text{O}_3$  with n/10 iodine.

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### (3). PRECIPITATION.

In the work given under this method for volumetric analysis, the student will prepare the standard solutions de-

scribed below, and will make the required determinations in the substances contained in Bottles Nos. 12, 13 and 14, and report upon the same as usual.

*N/10 Silver Nitrate.*

$\text{AgNO}_3 = 169.97$ .    16.997 grams per litre.

Weigh very carefully 4.2492 grams of the pure salt, dissolve in distilled water and dilute to 250 cc. The solution must be kept in a dark place, since it deteriorates under the action of light.

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*N/10 Sodium Chloride.*

$\text{NaCl} = 58.5$ .    5.850 grams per litre.

Weigh very carefully 2.925 grams of the pure salt, dissolve in distilled water and dilute to 500 cc.

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*N/10 Ammonium Sulpho-Cyanide.*

$\text{NH}_4\text{SCN} = 76.172$ .    7.6172 grams per litre.

The solution cannot be accurately prepared by weighing the salt, since it is deliquescent; therefore dissolve about four grams in 400 cc. of distilled water, and make the solution deci-normal by titration with n/10  $\text{AgNO}_3$ , according to the directions hereafter given.

---

*Titration of Silver Nitrate.*

(a) *With N/10 Sodium Chloride.*—Measure from the burette 25 cc. of n/10  $\text{NaCl}$  into a beaker, add two drops of normal potassium chromate indicator (See Indicators in Ap-

pendix.), and titrate with n/10  $\text{AgNO}_3$  till a faint, permanent red precipitate is formed.

(b) *With N/10 Ammonium Sulpho-Cyanide.*—Measure from the burette 25 cc. of n/10  $\text{AgNO}_3$  into a beaker, add three drops of ammonio-ferric alum indicator (See Indicators in Appendix.) and about 1 cc. of  $\text{HNO}_3$ ; titrate with n/10 sulpho-cyanide till a faint, permanent red color is produced.

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#### Bottle No. 12.—Sodium Chloride Solution.

To be titrated for Cl. N/10 factor for Cl = 0.003545.

Weigh very carefully in the weighing-flask about 0.500 grams of the solution, and dilute to 100 cc. with distilled water. Mix thoroughly and carefully measure out several samples of 20 cc. each. Titrate with n/10  $\text{AgNO}_3$ , using the chromate indicator.

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#### Bottle No. 13.—Silver Nitrate Solution.

To be titrated for Ag. N/10 factor for Ag = 0.010793.

(1) Weigh carefully from three to five grams of the solution and titrate with n/10 sulpho-cyanide without dilution.

(2) Weigh carefully from three to five grams of the solution, place it in a beaker and measure into it from a burette an excess of n/10  $\text{NaCl}$ ; add two drops of chromate indicator, mix thoroughly, and titrate the excess of  $\text{NaCl}$  with n/10  $\text{AgNO}_3$ .

**Bottle No. 14.—Hydrocyanic Acid Solution.**

HCN = 27.048. N/10 factor = 0.0054096.

This acid is highly poisonous and should be handled with care. So also is the solution in the bottle, which is made of KCN, not of the free acid. Weigh carefully about five grams of the solution in a tightly stoppered flask, and add a solution of KOH to decided alkalinity. Dilute largely and titrate the whole solution with n/10 AgNO<sub>3</sub>, until a slight, permanent precipitate is formed. The reaction is as follows: —2 KCN + AgNO<sub>3</sub> = KCN, AgCN + KNO<sub>3</sub>, in which a double cyanide of silver and potassium is in solution; but the addition of another drop of silver solution destroys the double cyanide and causes a precipitate of AgCN, according to the equation:—KCN, AgCN + AgNO<sub>3</sub> = 2 AgCN + KNO<sub>3</sub>.

## GRAVIMETRIC SEPARATIONS.

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The student is requested to analyze the substances in the boxes numbered from 1 to 4, according to the directions given, and report results.

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### Box No. 1.—Silver Coin.

Silver coin usually consists of silver and copper, with traces of lead and gold. Take a sample weighing about 0.250 grams, clean it by washing with KOH or NH<sub>4</sub>OH, then with water. Dry, cool and weigh accurately. Place it in the weighing-flask, dissolve it in the smallest adequate quantity of HNO<sub>3</sub>, cool and dilute to the mark.

Take 30 cc. of this solution, dilute with distilled water, heat to about 70° C., and gradually add HCl as long as a precipitate is formed and until HCl is in large excess; stirring after each addition. Place the beaker containing the precipitate in a dark place till the precipitate has settled; filter, wash first with hot distilled water acidulated with HNO<sub>3</sub>, then with distilled water alone, until filter-paper and precipitate are clean, reserving the filtrate and washings. From this point follow the directions in Gravimetric Determinations, for the determination of chlorine in barium chloride. From the weight of the silver chloride found, determine the per cent. of silver.

Boil the filtrate, remove the lamp and add, gradually and with constant stirring, KOH solution till strongly alkaline, boil for ten minutes and set aside till the precipitate is set-

tled. Filter off the clear liquid and wash the filter with hot water; add hot distilled water to the precipitate in the beaker, and boil again. Continue these operations until all traces of alkali are removed from the precipitate and from the filter which contains it. Cover the funnel and dry in the drying-oven; remove the precipitate from the filter to a piece of glazed paper as completely as possible, burn the filter, in the weighed capsule, to a white ash, cool, moisten with a drop or two of  $\text{HNO}_3$ , and carefully evaporate to dryness; add the bulk of the precipitate and ignite. Cool in the desiccator and weigh as cupric oxide. Report the per cent. of copper.

Titrate a portion of the original solution with n/10 sulphocyanide, as a check upon the gravimetric determination of silver. Copper, up to 70%, does not interfere.

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#### Box No. 2.—Brass.

Brass is an alloy of copper and zinc, usually containing traces of tin and lead. Weigh carefully about 0.500 grams of the clean, dry sample; dissolve in a beaker in the least adequate quantity of  $\text{HNO}_3$  (sp. gr. 1.40), add 25 cc. of distilled water and heat. If there is a residue, filter and wash with water containing 1%  $\text{HNO}_3$ .

Residue (a) =  $\text{SnO}_2$ . Dry, ignite in a porcelain capsule, cool and weigh as usual, and return the per cent. of metallic tin.

Filtrate (a) = Cu, Zn, Pb. To the filtrate add 3 cc. of  $\text{H}_2\text{SO}_4$ , evaporate in a porcelain dish till copious white fumes of  $\text{SO}_3$  are given off, cool and add 50 cc. of cold distilled water; if there is a residue, filter and wash with a small quantity of distilled water.

Res. (b) =  $\text{PbSO}_4$ . Dry, ignite to white ash, cool, moisten with a few drops of  $\text{H}_2\text{SO}_4$ , cover the capsule, heat moderately till excess of  $\text{H}_2\text{SO}_4$  is driven off, then ignite strongly. Cool and weigh as usual, and report the per cent. of lead.

Filt. (b) = Zn, Cu. The united filtrate and washings are diluted with distilled water to about 100 cc.; add 1 cc. of  $\text{H}_2\text{SO}_4$  and boil; while boiling add, gradually and at intervals, a solution of sodium thio-sulphate, as long as a black precipitate continues to form; avoiding a large excess and boiling after each addition of thio-sulphate. Filter and wash thoroughly with hot water.\*

Res. (c) =  $\text{Cu}_2\text{S}$ . Dry, remove the precipitate from the filter to a piece of glazed paper, ignite the filter thoroughly, cool, add the precipitate together with an equal bulk of sulphur; mix thoroughly, cover the crucible and ignite, moderately at first, but finishing with a dull, red heat; all of the sulphur will be burnt off in about five minutes. There will remain in the capsule a mixture of  $\text{CuO}$ ,  $\text{Cu}_2\text{S}$ ; as these salts contain practically the same per cent. of copper, the weight found may be considered as  $\text{Cu}_2\text{S}$ . Report the per cent. of copper. Check this result by dissolving the mixture in the capsule with strong  $\text{HNO}_3$  or aqua regia, and determining the copper by one of the methods given in Part 2, under Analysis of Copper Ores.

Filt. (c) = Zn. Divide the solution in two equal parts. Part (1) acidify with  $\text{HNO}_3$ , evaporate to small bulk, filter to remove separated sulphur, transfer to a large *porcelain* evaporating-dish, and boil down to about 25 cc.; add a solu-

\*Fresenius, page 540; Classen, page 51. Separation of copper from barium, strontium, calcium, magnesium, aluminum, chromium, zinc, manganese, nickel, cobalt and iron.

tion of  $\text{NaHCO}_3$ , till strongly alkaline, boil, wash by decantation to remove alkalies as completely as possible, and wash again on the filter with hot water. Part (2) place in a casserole, evaporate to dryness, and heat on the sand-bath until no fumes of  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$  come off, cool and dissolve in the least adequate quantity of water. Transfer to a beaker; when the solution should be only very faintly acid, and should not exceed 20 cc. in volume. Add sufficient excess of a 25% solution of neutral potassium oxalate to redissolve the precipitate formed; boil, and add gradually and with stirring, a quantity of strong acetic acid equal to the volume of the solution. Boil ten minutes, allow to settle, and add more acetic acid to test for further precipitation. Let stand five hours, filter, and wash with a solution of equal parts of water, alcohol and acetic acid, until a drop of the filtrate shows no residue on evaporation.

Res. (d) = (1)  $\text{ZnCO}_3$ , (2)  $\text{ZnC}_2\text{O}_4$ . Dry, incinerate the filter alone, add the bulk of the precipitate, and ignite to  $\text{ZnO}$ . Cool, weigh, and determine the per cent. of zinc in each.

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### Box No. 3.—Paris Green.

Pure Paris Green is an aceto-arsenite of copper, of the formula:  $3(\text{CuO}, \text{As}_2\text{O}_3), \text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$ . Dry the sample at  $100^\circ \text{ C.}$ , cool and carefully weigh about one gram; place in a beaker, add cold  $\text{NH}_4\text{OH}$  and stir till all of the green particles are dissolved. If there is a residue, filter through counterpoised filters and wash very thoroughly with hot water.

Residue (a) = Insoluble matter. Dry at  $100^\circ \text{ C.}$ , cool and weigh.

Filtrate (a) = Cu, As. Add HCl till nearly neutral, then add yellow ammonium sulphide in considerable excess and digest at a moderate heat for a half hour. Decant the supernatant liquid on a filter, add more ammonium sulphide to the residue in the beaker, and digest again; filter and wash with distilled water to which a little ammonium sulphide has been added. Evaporate the filtrate quite low and, if more CuS appears, filter. If  $\text{As}_2\text{S}_3$  comes down, dissolve it in ammonium sulphide.

Res. (b) = CuS. Dry, ignite and weigh; following the method given in the analysis of brass. Report the per cent. of copper.

Filt. (b) = As. Cautiously add dilute HCl to acid reaction; warm, pass  $\text{H}_2\text{S}$  gas through the warm solution for a half hour, filter, reject the filtrate, dissolve the precipitate in KOH and filter to remove free sulphur. Pass chlorine gas into the solution for one hour, keeping the solution alkaline; acidulate with HCl, upon which the solution must remain clear; add excess of  $\text{NH}_4\text{OH}$ , then magnesia mixture (Reagent 3.) in excess, and let stand for twelve hours. Filter through a weighed filter (or through counter-poised filters), wash well with a mixture of one part of  $\text{NH}_4\text{OH}$  and three parts distilled water.

Res. (c) =  $\text{MgNH}_4\text{AsO}_4 + 6\text{H}_2\text{O}$ . Dry at  $102^\circ$  to  $103^\circ$  C., and weigh; repeat the drying till constant weight is obtained. The result should consist of  $(\text{MgNH}_4\text{AsO}_4)_2 \cdot \text{H}_2\text{O}$ . Report the per cent. of arsenic.

Check this result by igniting the precipitate to the pyroarsenate and weighing in that form, as follows: Carefully remove the precipitate from the filter as completely as possible, cut the filter into small pieces, place them in the capsule, moisten with a solution of  $\text{NH}_4\text{NO}_3$ , dry and ignite.

When cold, add the precipitate, moisten with  $\text{HNO}_3$ , dry at  $100^\circ \text{ C}.$ , then ignite strongly for ten minutes, cool and weigh as  $\text{Mg}_2\text{As}_2\text{O}_7$ .

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#### Box No. 4.--Baking Powder.

The value of baking powder depends upon (1) the amount of  $\text{CO}_2$  which a given weight of the powder will give off when dissolved in water, (2) the solution thus formed being neutral, and (3) the purity of the powder.

The following tables will show the composition of some of the baking powders in common use:—

No. 1.

Corn Starch .....	4%
Bitartrate of Potash.....	58%
Bicarbonate of Soda .....	38%

No. 3.

Flour.....	37.5%
Tartaric Acid .....	25. %
Bicarbonate of Soda .....	37.5%

No. 2.

Corn Starch .....	37%
Tartaric Acid .....	10%
Bicarbonate of Soda .....	30%
Sesqui-carb. of Amm.....	6%
Alum .....	17%

No. 4.

Flour .....	20%
Bitartrate of Potash .....	51%
Tartaric Acid .....	3%
Bicarbonate of Soda.....	24%
Carbonate of Ammonia ...	2%

These are known as tartaric acid or cream of tartar powders; the alum in No. 2 is probably used to make the bread white and performs no other part in the powder. There are, besides the foregoing powders, those which have no tartaric acid, such as

- (1) The alum powders, which should always be rejected.
- (2) The phosphate powders, which are said to be among the best.

The following directions for analysis apply only to the tartaric acid or cream of tartar powders. These should

always be tested for adulterations, especially alum; this, if present, should be determined.

(a) *Determination of Starch or Flour.*—Take 0.500 grams of the powder, add cold distilled water and shake till the powder is dissolved; filter on tared filters, dry at 100° C., and weigh. (Impurities, such as phosphate of lime, if present, will vitiate results; if such impurities are discovered, the starch may be converted to sugar by boiling with dilute acid for several hours, and the sugar determined by Fehling solution.)

The filtrate from the starch should, after boiling, give a neutral reaction with litmus. If, as is often the case, it gives an alkaline reaction, titrate this excess of alkali with n/10  $H_2SO_4$ , and calculate the alkali found as  $NaHCO_3$ .

(b) *Determination of Soda and Potash.*—First test for potassium with the flame. Take one gram of the powder, incinerate thoroughly in a porcelain evaporating dish, till the carbon is all burnt off. The mass must not be fused. Extract the residue with hot water, and filter into a flask. The filtrate should not exceed 30 cc. If there is no potash present, titrate this filtrate for soda with n/10  $H_2SO_4$ . If potash is present, place the flask containing the filtrate over the lamp and boil; while boiling, add gradually from a burette normal tartaric acid until the red color of the indicator fails to appear after boiling two minutes; now add as much more of the normal tartaric acid, cool the solution and proceed according to the method given for the determination of potash in Bottle No. 5, in Volumetric Analysis.

(c). *Determination of  $CO_2$ .*—(1) Use the ordinary carbonic acid apparatus as described under Gravimetric Determinations. Weigh about 0.500 grams of the powder and

treat it in the apparatus, displacing the  $\text{CO}_2$  with dilute  $\text{H}_2\text{SO}_4$ . This will give the *total* carbonic acid.

(2) Determine the amount of  $\text{CO}_2$  which the powder will give off when dissolved in water alone, using the same apparatus. At the last of the operation, heat the flask and contents to  $80^\circ \text{ C}.$ , and cool before weighing. This result will give the available carbonic acid.

(d) *Determination of Tartaric Acid.*—Since the tartaric acid cannot be advantageously determined by any direct process, we resort to an indirect method by calculation, as follows:—

If the tartaric acid exists in the powder in the form of bi-tartrate of potash, the following proportion will give the amount of that salt which the powder contains:— $\text{KOH} : \text{C}_4\text{H}_5\text{KO}_6 :: \% \text{ KOH} : x$ ; in which x equals the per cent. of potassium bi-tartrate.

If there is no potash present in the powder, then we may conclude that the tartaric acid exists as such in the powder, and its per cent. may be thus calculated. Deduct from the total  $\text{NaOH}$  as found by (b) the excess, if any, of  $\text{NaOH}$  found by (a), and the difference will represent the amount of  $\text{NaOH}$  neutralized by the tartaric acid. The tartaric acid corresponding to  $\text{NaOH}$  neutralized may be calculated as follows:— $2\text{NaOH} : \text{C}_4\text{H}_6\text{O}_6 :: \% \text{ NaOH} : y$ , y equalling the per cent. of tartaric acid.

Report the composition of the powder as follows:—

Starch or Flour.....	%
Total $\text{NaHCO}_3$ .....	%
Excess of $\text{NaHCO}_3$ .....	%
Bitartrate of Potash ( $\text{C}_4\text{H}_5\text{KO}_6$ ) or.....	%
Tartaric Acid ( $\text{C}_4\text{H}_6\text{O}_6$ ).....	%

If any impurities are present in the powder, they should also be determined and reported.

## INTERNATIONAL ATOMIC WEIGHTS, 1903.

		O = 16.	H = 1.			O = 16.	H = 1
Aluminium.	Al	27.1	26.9	Molybdenum ..	Mo	96.0	95.3
Antimony...	Sb	120.2	119.3	Neodymium ..	Nd	143.6	142.5
Argon.....	A	39.9	39.6	Neon... . . .	Ne	20.0	19.9
Arsenic.....	As	75.0	74.4	Nickel ... . .	Ni	58.7	58.3
Barium.....	Ba	137.4	136.4	Nitrogen... . .	N	14.04	13.93
Bismuth.....	Bi	208.5	206.9	Osmium. ....	Os	191.0	189.6
Boron.....	B	11.0	10.9	Oxygen.....	O	16.00	15.88
Bromine.....	Br	79.96	79.36	Palladium. ....	Pd	106.5	105.7
Cadmium.....	Cd	112.4	111.6	Phosphorus. . .	P	31.0	30.77
Cæsium.....	Cs	133.0	132.0	Platinum . ....	Pt	194.8	193.3
Calcium ...	Ca	40.1	39.8	Potassium . . .	K	39.15	33.86
Carbon.....	C	12.00	11.91	Praseodymium	Pr	140.5	139.4
Cerium. ....	Ce	140.0	139.0	Radium.....	Ra	225.0	223.3
Chlorine.....	Cl	35.45	35.18	Rhodium .. . .	Rh	103.0	102.2
Chromium... .	Cr	52.1	51.7	Rubidium. ....	Rb	85.4	84.8
Cobalt.....	Co	59.0	58.56	Ruthenium ...	Ru	101.7	100.9
Columbium (Niobium) ..	Cb	94.0	93.3	Samarium .. . .	Sm	150.0	148.9
Copper.....	Cu	63.6	63.1	Scandium .. . .	Sc	44.1	43.8
Erbium.....	E	166.0	164.8	Selenium. ....	Se	79.2	78.6
Fluorine... . .	F	19.0	18.9	Silicon .. . . .	Si	28.4	28.2
Gadolinium.	Gd	156.0	155.0	Silver .. . . .	Ag	107.93	107.12
Gallium... . .	Ga	70.0	69.5	Sodium .. . . .	Na	23.05	22.88
Germanium..	Ge	72.5	71.9	Strontrium. ....	Sr	87.6	86.94
Glucinum (Beryllium).	Gl	9.1	9.03	Sulphur. ....	S	32.06	31.83
Gold.....	Au	197.2	195.7	Tantalum. ....	Ta	183.0	181.6
Helium.....	He	4.0	4.0	Tellurium. ....	Te	127.6	126.6
Hydrogen... .	H	1.008	1.000	Terbium. ....	Tb	160.0	158.8
Indium.....	In	114.0	113.1	Thallium. ....	Tl	204.1	202.6
Iodine.....	I	126.85	125.90	Thorium. ....	Th	232.5	230.8
Iridium.....	Ir	193.0	191.5	Thulium. ....	Tm	171.0	169.7
Iron.....	Fe	55.9	55.5	Tin .. . . . .	Tn	119.0	118.1
Krypton.....	Kr	81.8	81.2	Titanium. ....	Ti	48.1	47.7
Lanthanum ..	La	138.9	137.9	Tungsten. ....	W	184.0	182.6
Lead.....	Pb	206.9	205.35	Uranium. ....	U	238.5	236.7
Lithium.....	Li	7.03	6.98	Vanadium. ....	V	51.2	50.8
Magnesium ..	Mg	24.36	24.18	Xenon .. . . .	X	128.0	127.0
Manganese...	Mn	55.0	54.6	Ytterbium. ....	Yb	173.0	171.7
Mercury.....	Hg	200.0	198.5	Yttrium. ....	Yt	89.0	88.3
				Zinc. .... . .	Zn	65.4	64.9
				Zirconium. ....	Zr	90.6	89.9

The Atomic Weights used in this book are taken from the first column of figures in the above list, the basis for which is Oxygen = 16.

Those using the above table should be careful that they do not confound the two systems.

PART TWO

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SELECT METHODS

IN

QUANTITATIVE ANALYSIS

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FOR THE USE OF ADVANCED STUDENTS  
AND PRACTICING CHEMISTS



## PREFACE TO PART TWO.

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This portion of the work was first published by Professor Cheever in a separate volume, containing a number of methods in inorganic quantitative analysis, which he had carefully worked out and which were ratable among the most improved methods in use at that time. In the three editions which have been published by the writer since the regretted death of Professor Cheever, the progress of the science of chemistry has necessitated an almost entire change of this part of the work, in order that the book may contain nothing but the most modern practice at the time of issue. This has resulted in the elimination of nearly all of the matter originally contained in the book; but an unfailing sense of his former kindness and a sincere regard for his many admirable qualities of mind and heart are but faintly emphasized in the continued use of Professor Cheever's name as the author.

Very few, if any, of the methods herein given can be wholly accredited to any particular chemist; but have been improved and re-improved by succeeding workers in reaching their present condition, until it is difficult to decide to whom credit is due. The writer has endeavored to give full

credit, where it has been possible, to those chemists whose work it has been necessary to quote. As in the former edition, he wishes to gratefully acknowledge a particular indebtedness to Mr. Oscar Textor (like the writer, an old friend and former assistant of Professor Cheever), whose professional card is gladly given place in this book, and to render thanks for assistance to Mr. R. F. Flintermann and Mr. A. J. Morse.

FRANK CLEMES SMITH.

HARRISBURG, ARIZONA, Nov. 1st, 1904.

# SELECT METHODS IN QUANTITATIVE ANALYSIS.

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NOTE.—Before taking up the following work, the chemist is requested to read the article in the Appendix on Use of Platinum Vessels. Reagents referred to by number will be also found in the Appendix.

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## Analysis of Limestone.

Pulverize a few grams in an agate mortar and dry at 100° C. Weigh one gram of the dried sample, transfer to a casserole, cover with a cover-glass, add 20 cc. of distilled water, 10 cc. of HCl and 2 cc. of HNO<sub>3</sub>; when effervescence ceases, wash the cover-glass into the solution and evaporate to dryness. Cool, moisten with HCl (sp. gr. 1.12), add water, and again evaporate to dryness. Cool, moisten again with HCl (sp. gr. 1.12), take up with water, boil and filter.

*Residue (a) = Silica and Silicates.*—Dry the filter and contents. If a considerable amount of bases is present, the precipitate should be removed from the filter, the filter burnt to ash, the precipitate added thereto, and the whole fused in a platinum crucible with Na<sub>2</sub>CO<sub>3</sub>. Dissolve in water slightly acidulated with HCl, in a casserole, cleaning out crucible by means of HCl and adding washings to casserole. Acidulate with HCl, evaporate to dryness, cool, moisten with HCl and water, and evaporate to dryness again. Cool, moisten with HCl, add 10 cc. of water and allow to digest for some time.

Dilute with water, filter, wash *well* with hot water, adding the filtrate to filtrate (*a*) below. Dry the precipitate, ignite, cool and weigh. Treat in the crucible with 2 cc. of HF and a few drops of  $H_2SO_4$ ; evaporate to dryness, ignite, cool and weigh again. The loss in weight equals the  $SiO_2$ . If there still remains a notable residue in the crucible, it should be further examined.

*Filtrate (a).*—Add 10 cc. of HCl, boil and add  $NH_4OH$  to slight alkaline reaction, then boil again; allow to subside, filter hot and wash twice on the filter, reserving filtrate and washings. Dissolve the residue on the filter with a few drops of dilute HCl, receiving the solution in the beaker in which precipitation was made, and washing the filter well with hot water. Dilute the solution, boil and re-precipitate with  $NH_4OH$ ; wash by decantation and add filtrate to filtrate (*b*).

*Res. (b) = Iron, Alumina and Phosphoric Acid.*—In ordinary analyses of limestone, this residue is dried, ignited, cooled and weighed; and the result reported as mixed oxides of iron and alumina. If it is desired to obtain the actual per cent. of iron, a 2 or 3-gram sample of the limestone is first ignited (to destroy organic matter), then dissolved in HCl, and the iron determined volumetrically. Alumina may also be determined, in a similar sample, according to the method given under Analysis of Iron Ores.

*Filt. (b).*—Concentrate this solution by boiling to 250 cc., add, with constant stirring, 30 cc. of a boiling, saturated solution of  $(NH_4)_2C_2O_4$  (there must be sufficient to form oxalates of both calcium and magnesium), and set aside in a warm-place for one-half hour. If there is any question as to the complete separation of the magnesium, this residue

may be washed on the filter (reserving filtrate and washings), dissolved on the filter in dilute HCl, the filter washed, a little ammonium oxalate and excess of NH<sub>4</sub>OH added to the solution, and the solution boiled, filtered and washed by decantation; adding filtrate and washings to reserved filtrate.

*Res. (c) = Calcium Oxalate.*—Dry and ignite with blast-lamp to CaO, repeating the ignition, cooling and weighing until weight is constant.

In this precipitate of calcium oxalate, the calcium may be determined volumetrically, as follows:—Remove the wet filter containing the precipitate from the funnel and spread it on the inside (not bottom) of a No. 4 beaker. Wash the precipitate off the filter with a hot solution containing one part H<sub>2</sub>SO<sub>4</sub> and three parts water, leaving the filter on the side of the beaker. Dilute with warm water to about 250 cc. and titrate with n/10 KMnO<sub>4</sub>. At the close of the operation, push the filter down into the solution and add final KMnO<sub>4</sub> to color. The n/10 factor for CaO is 0.002805.

*Filt. (c).*—This solution should not be over 350 cc. in bulk, and must be made thoroughly cold. Add 15 cc. of strong NH<sub>4</sub>OH and 15 cc. of solution of Na<sub>2</sub>HPO<sub>4</sub>, and mix thoroughly, keeping the stirring-rod away from the sides of the beaker; set aside in a cool place for 1½ to 2 hours. If the above solution can be agitated with an air-current during precipitation, it will be complete in 20 minutes. If, in concentrating the original solution, or upon addition of strong NH<sub>4</sub>OH, a precipitate occurs, it must be dissolved in HCl, and the solution again made alkaline with ammonia. Filter and wash with water containing 20 to 25% NH<sub>4</sub>OH.

*Res. (d) = Mg<sub>2</sub>(NH<sub>4</sub>)<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>.*—Dry and ignite, commencing with a low heat and finishing with blast. If the

residue is not white, add a few drops of dilute  $\text{HNO}_3$ , evaporate to dryness and ignite, cool and weigh till weight of magnesium pyro-phosphate is constant.

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*Determination of  $\text{CO}_2$ .*—Fuse two grams of vitrified borax in a platinum crucible, cool and weigh. Repeat to constant weight. Add about 0.500 grams of the well-dried limestone and weigh. Apply heat gradually and finally heat to fusion; cool and weigh. The loss equals  $\text{CO}_2$ .

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*Determination of Phosphorus.*—Dissolve 5 grams in HCl (sp. gr. 1.12) evaporate to dryness, moisten with HCl and take up with water; filter, add 5 to 10 drops of ferric chloride, and precipitate with  $\text{NH}_4\text{OH}$ ; boil, filter, wash, and dissolve precipitate on the filter with 20 cc. of hot dilute  $\text{HNO}_3$ . Wash filter into solution with hot water, dilute and again precipitate with  $\text{NH}_4\text{OH}$ , filter and wash. Re-dissolve on the filter with hot dilute  $\text{HNO}_3$ , wash filter into solution, add 30 cc. of molybdate solution (Reagent 6-b), shake well and let stand two hours at 80° C. Filter and wash with water containing one per cent.  $\text{HNO}_3$ . Determine the phosphorus in this residue by one of the methods given under Analysis of Iron Ores. If it is desirable to examine the insoluble residue, it may be fused with  $\text{Na}_2\text{CO}_3$ , after ignition, the fusion taken up with water and a little HCl, filtered, and the solution added to the solution of the first precipitate above.

(Mr. Textor states that, after filtering off insoluble residue, if the HCl solution be concentrated to from 5 to 7 cc. and 30 cc. of water added, the phosphorus may be precipitated with molybdate in that solution.)

### Analysis of Iron Ores.

The ore should be accurately sampled, and the sample finely pulverized and dried at 100° C.

*Determination of Iron. Method (1).*—Pulverize two or three grams of the sample very finely, in an agate mortar, and dry at 100° C. Take exactly 0.559 grams, place it in a No. 1 beaker (without lip), add 25 cc. of strong HCl, cover with a watch-glass, digest at 90° to 100° C. till dissolved and the residue appears white and flocculent. (See note below.) To the hot solution add solution of SnCl<sub>2</sub> (Reagent 4), drop by drop, to the exact point where the solution just becomes colorless; pour the solution and washings of the beaker into a No. 5 beaker, dilute largely with water, add 30 cc. of HgCl<sub>2</sub> solution (Reagent 5) and titrate with n/10 K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. Each cc. of n/10 K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> = 1% of iron.

**NOTE.**—Most iron ores are completely soluble in strong HCl at a low heat, but it may be necessary to finish the solution of the ore by incipient boiling, in which case great care must be taken that no ferric chloride is lost by volatilization. Many chemists make the solution of the ore in a flask provided with a condensing-tube; this method, however, is not convenient, and is not generally necessary.

Samples set aside over night, to digest with strong HCl without heat, are frequently found to be almost completely dissolved. Should the residue after solution appear to be incompletely decomposed and have a dark color, it must be filtered off, fused with Na<sub>2</sub>CO<sub>3</sub>, taken up with HCl, and the filtrate therefrom added to the first filtrate before reducing and titrating.

If the iron in fused residues is titrated separately, it is frequently the case that organic matter prevents the decolorization in the reduction by SnCl<sub>2</sub>, and too much of that reagent is added. It is safer to precipitate the iron from the solution of the fusion with NH<sub>4</sub>OH, and then re-dissolve on the filter in HCl, without washing; in this solution SnCl<sub>2</sub> will effect a sharp decolorization.

Ores containing a large amount of organic matter are first ignited, before proceeding with the regular process of solution. If the

amount of organic matter is small, or if the ore is pyritous, the ore is dissolved in HCl with addition of potassium chlorate, after which the regular method is followed.

Where many examinations of iron ore are to be continually made, it will be found good policy to keep on hand a supply of standard iron ore, whose various constituents have been carefully determined, in various ways, so that they are exactly known. In making analyses of ores, for various ingredients, if a sample of the standard ore be similarly treated, at the same time, it will be found a valuable check upon the rectitude of the standard solutions used and the methods employed.

Many iron ores which are only partially soluble in HCl yield if digested with solution of  $\text{SnCl}_2$  (Reagent 4) and HCl. If excess of  $\text{SnCl}_2$  is added, beyond an amount sufficient to reduce the iron, the solution may be brought back to the red or yellow ferric color by addition of  $\text{KMnO}_4$ ; it is then just decolorized by  $\text{SnCl}_2$ , excess of  $\text{HgCl}_2$  is added and the titration made with  $\text{K}_2\text{Cr}_2\text{O}_7$ .

*Method (2), by Zimmermann-Reinhardt.*

The principal claim to advantage of this method over the one just given, lies in the statement that the titration with permanganate consumes less time than that with bi-chromate. Although this may be true, such advantage is more than offset by the constant deterioration of permanganate solutions; while bi-chromate solutions may be said to be absolutely stable. In this method, the ore is dissolved in dilute HCl with the aid of  $\text{SnCl}_2$ , the iron reduced by  $\text{SnCl}_2$ , whose excess is taken up with  $\text{HgCl}_2$ , a solution containing  $\text{MnSO}_4$  and phosphoric acid is added (the former to counteract the chlorine formed by oxidation of HCl, the latter to unite with iron to facilitate observation of the end reaction), the solution diluted and titrated with permanganate.

Place 0.600 grams of the prepared sample in a No. 0 lipless beaker, add 2.5 cc. of  $\text{SnCl}_2$  (Reagent 20-a) and 10 to 15 cc. of HCl (Reagent 20-b), cover with a glass, and boil gently to complete solution. The solution will generally be complete in a few minutes; while still hot, carefully add additional drops of  $\text{SnCl}_2$  (Reagent 20-a) until the iron is just reduced to the ferrous state, as indicated by the disappearance of the greenish-yellow color. During this reduction the solution is constantly agitated by giving the beaker

a rotating motion. The sides of the beaker are then washed down, and 5 cc. of solution of  $HgCl_2$  (Reagent 20-c) are added. Wash the solution into a No. 5 beaker, in which has been placed 6 to 8 cc. of a solution of  $MnSO_4$  (Reagent 20-d), mix and titrate with standard  $KMnO_4$  (Reagent 20-e).

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*Determination of Silica. Method (1).*—Dissolve one gram of the sample in a No. 4 casserole, in strong HCl, add about 5 cc. of strong  $H_2SO_4$  and evaporate till  $SO_3$  fumes arise; maintain at this temperature for a time to decompose silicates, dissolve in water, filter, wash, ignite in a weighed crucible. After weighing the crucible and residue, add 5 drops of  $H_2SO_4$ , a few drops of water, and HF according to the quantity of the residue. After visible action ceases, expel the acids by evaporation, ignite and weigh. Repeat the treatment with HF if necessary. The loss in weight equals the silica.

*Method (2).*—Take one gram of the prepared sample, dissolve in a beaker or casserole with strong HCl, and evaporate to dryness. Cool, moisten with HCl and a little water, and again evaporate to dryness. Cool, moisten with HCl and take up with water; filter, wash, dry and ignite the residue. Fuse the residue in a platinum crucible with  $Na_2CO_3$ , take up in very dilute HCl and evaporate to dryness; take up again in very dilute HCl and again evaporate to dryness; take up again, in the same manner, filter, wash, dry, ignite and weigh.

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*Determination of Manganese. Method (1).*—Dissolve about two grams of the ore in strong HCl. For hematites

containing less than one per cent. of manganese, add 5 to 10 drops of  $\text{HNO}_3$  (sp. gr. 1.20), to oxidize ferrous iron; for magnetites add more  $\text{HNO}_3$ . Boil down to 10 or 15 cc., transfer to a 500 cc. flask, dilute to 300 cc., add a slight excess of  $\text{ZnO}$ , (Reagent 16), and, when precipitation is complete, dilute to the mark, mix well, filter through a large ribbed filter, take 300 cc. in a 500 cc. flask, boil and titrate with n/10  $\text{KMnO}_4$ . n/10 factor for Mn = 0.00165.

When the percentage of manganese is low, and when it is approximately known (as in working duplicate samples), add the  $\text{KMnO}_4$  solution almost to the required quantity, shake and make the final addition carefully. Where there is much manganese (as in spiegel or ferro) the  $\text{KMnO}_4$  solution should be added in portions of about 10 cc. at a time, shaking after each addition, and finally proceeding cautiously to the end reaction. The use of  $\text{Na}_2\text{CO}_3$ , before the precipitation with  $\text{ZnO}$ , is not only unnecessary but objectionable.

*Method (2).*—The ore is dissolved in HCl and the HCl driven off by evaporation with  $\text{H}_2\text{SO}_4$ . In other respects it is the same as the method above given.

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*Determination of Sulphur.* *Method (1).*—Fuse 3 grams of the ore with fusing mixture (Reagent 1), using about six or eight parts of the reagent to one part of the ore. Extract the fusion with hot water, add HCl in excess and a few drops of bromine. Evaporate to dryness, moisten with HCl, take up in water, filter and wash. Precipitate the iron in the filtrate by addition of excess of  $\text{NH}_4\text{OH}$ , mix well and (without filtration) add a boiling solution of  $\text{BaCl}_2$  and mix. Then add sufficient HCl to the mixture to dissolve the ammonia precipitate. Cool and filter, washing with water con-

taining from 5 to 10% of HCl. Filter, wash, dry, ignite and weigh.

*Method (2).*—Mix thoroughly in the crucible 3 grams of finely pulverized ore, 2 grams of MgO and 1 gram of Na<sub>2</sub>CO<sub>3</sub>; heat to redness, *without fusing*, for ten minutes, cool, add water and 1 cc. of bromine, boil, filter, acidify with HCl, and precipitate with a boiling solution of BaCl<sub>2</sub>.

\**Method (3).*—Place three grams of the fine, dry ore in a porcelain dish, add about one-half gram of pulverized KClO<sub>3</sub>, pour over it 50 cc. of HNO<sub>3</sub> (sp. gr. 1.42) and cover with a cover-glass; raise the heat gradually and boil for fifteen minutes, adding from time to time crystals of KClO<sub>3</sub>; remove the cover and evaporate to small bulk, add strong HCl and evaporate to dryness on the water-bath. Moisten the residue with strong HCl, add water, boil, filter and wash thoroughly; nearly neutralize the filtrate with NH<sub>4</sub>OH, boil, add 5 cc. of tartaric acid solution, (Reagent 13), and sufficient BaCl<sub>2</sub> solution, boil, let stand all night, filter, wash thoroughly with hot water, then with dilute solution of ammonium acetate to dissolve any possible barium nitrate. Ignite and weigh as usual.

*Method (4).*—Place three grams of the fine, dry ore in a four-ounce Erlenmeyer flask, moisten thoroughly with the smallest quantity of water, add about three cc. of bromine and shake well; heat to 80° C. for five minutes, add 15 cc. of strong HCl and continue the heat fifteen minutes longer; transfer to a porcelain dish and evaporate to dryness on the water-bath. Take up in HCl and water, boil, filter, wash thoroughly; nearly neutralize filtrate with NH<sub>4</sub>OH, boil and proceed as in method above.

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\*Crookes, page 480.

*Determination of Phosphorus. Method (1).*—(Mr. Textor's modification of Wood's Direct Method.) Dissolve 3.26 grams of the finely pulverized and dried ore in HCl, evaporate to dryness and heat on the hot-plate for three hours. Dissolve in 15 cc. of HCl, add an equal bulk of water and filter into a No. 3 beaker; washing the filter three or four times. Concentrate the filtrate to a point just short of separation of the oxide (or until excess of the acid is removed); cool and dilute to 40 cc. with water, stir well and add 75 cc. of molybdate solution (Reagent 6). Burn the insoluble residue in a platinum crucible, using the blast for one or two minutes; cool, add from 6 to 12 cc. of  $H_2SO_4$  (according to the quantity of the residue) and 5 cc. of HF, and evaporate till  $SO_3$  fumes arise. Cool, add 3 cc. of strong HCl, heat for five minutes, add water, heat to boiling and filter by itself; not into the main solution. This solution frequently has to be re-filtered till clear, as the fine residue is apt to run through the filter. The filter need be washed but three times with a small amount of water, and the bulk of the filtrate should not exceed 15 cc. Add this filtrate from the insoluble residue to the main solution, stir and let stand over night. Filter and wash seven times with water containing 2%  $HNO_3$ , dry and proceed as in the following method, noting the fact that a double weight of ore is used in the method just given.

*Method (2).*—(Mr. Textor's former method.)—Dissolve 1.63 grams of the ore in 40 cc. of HCl, (sp. gr. 1.20), evaporate to a moist residue in a No. 4 beaker or casserole, or one-half of the solution may remain liquid. Add 10 or 15 cc. of HCl (sp. gr. 1.20) and evaporate until the solution cannot be further concentrated without separation of the basic salt. Add an equal bulk of water, filter and wash the paper three or four times with as little water as possible con-

taining two per cent. of  $\text{HNO}_3$  (sp. gr. 1.20). Warm the filtrate to  $50^\circ$  or  $60^\circ$  C. and add 75 cc. of molybdate solution, (Reagent 6). Fuse the insoluble residue with  $\text{Na}_2\text{CO}_3$ , dissolve in HCl (sp. gr. 1.06) in a No. 6 evaporating dish. Evaporate to dryness and heat to expel all HCl; cool, moisten with the smallest adequate quantity of HCl, and take up in the smallest adequate quantity of water. Filter into the solution to which the molybdate has been added and let stand over night. Filter through a weighed Swedish filter (7 cm. diameter), dry at  $135^\circ$  C. for fifteen or twenty minutes. Weigh quickly, one minute after taking from the drying-oven; the filter paper having been previously dried and weighed in the same manner. The weight of the yellow precipitate contains 1.63 per cent. of phosphorus, so that each milli-gram equals 0.001 per cent. of phosphorus on the basis of the weight taken.

NOTE I.—The silica may also be determined from the fused residue. This method is applicable to Lake Superior and similar iron ores, free from titanium. It checks very closely with older methods, where the HCl is replaced by  $\text{HNO}_3$ .

NOTE II.—To avoid the necessity of the tedious fusion of residues in order to recover the insoluble phosphorus, Mr. C. T. Mixer\* proposes to place the insoluble residue, with its filter, in a platinum crucible, and, after burning off the paper, ignite at a red heat for a couple of minutes, breaking up the residue with a platinum rod. The ignited residue is then treated with a little water and a half dozen drops of HCl or  $\text{HNO}_3$ , boiled from three to five minutes and filtered; the filtrate contains all the insoluble phosphorus and is ready for precipitation with molybdate solution.

*Method (3).*—Dissolve two grams of the ore in 20 cc. of strong HCl in a No. 2 beaker, filter, slightly wash the residue and incinerate it, with the filter, in a platinum crucible; fuse with  $\text{Na}_2\text{CO}_3$ , take up with dilute HCl and water, add

\*Eng. and Mining Jour. Vol. LXII, page 4.

the filtrate to the first filtrate. Evaporate quite low, add 30 cc. of strong  $\text{HNO}_3$ , and evaporate to a syrupy consistence; add 30 cc. of  $\text{HNO}_3$  (sp. gr. 1.20) and boil. Proceed from this point as directed for making the yellow precipitate, etc., by Method (2), above, or by one of the following methods.

*Method (4).—Mr. Handy's Volumetric Method.*—See Analysis of Iron and Steel, Determination of Phosphorus, for a full description of this valuable method, and its application to iron ores. See also Note (1) thereunder.

*Method (5).—Mr. Emmerton's Volumetric Method.*—See Analysis of Iron and Steel, Determination of Phosphorus.

*Method (6).—The Magnesia Precipitation Method.*—See Phosphorus in Iron Ores and Products.

*Method (7).—Rapid Determination of Phosphorus.*—\*To 5 grams of the sample, previously pulverized and dried at  $100^{\circ}$  C., in a round-bottomed evaporating-dish, add 60 cc. of  $\text{HCl}$  (sp. gr. 1.20), cover and place on a tripod carrying a piece of asbestos board about seven inches square and one-quarter of an inch thick, through the center of which is cut a round hole two inches in diameter, in which the bottom of the dish may rest. Apply the full heat of a Bunsen burner to the bottom of the dish; the upper edges will be kept cool and will condense the steam formed, thus washing down the crust which would ordinarily form and which is a frequent source of difficulty when evaporating with nitric acid. Solution of the ore and evaporation in the covered dish to a volume not exceeding 15 cc. may be accomplished within 20 minutes. At this point, lower the flame, push the cover aside, and add 35 cc. of strong  $\text{HNO}_3$ ; replace the cover, and again evaporate with strong heat to about 15 cc. During both

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\*Journal Analyt. Chem. VI. 483.

evaporations it is well to have a stout wire twisted into a fork, whereby the dish may be lifted and its contents given an occasional whirl about the circumference. At the end of the second evaporation only traces of HCl will remain, which do not interfere with the precipitation of phosphoric acid. Dilute the solution to about 35 cc., filter while still hot, with the pump, into a shaking-flask. Place residue and filter at once in a platinum crucible, and ignite over the blast-lamp. Cool by aid of the blast, add sodium carbonate and fuse to perfect fluidity over the blast-lamp. Allow the cold blast to play upon the crucible for a minute, then plunge crucible and contents into about 25 cc. of  $\text{HNO}_3$  (sp. gr. 1.135), which has been previously placed in the dish in which the original solution was effected. Cover the dish and heat to boiling, and the fusion will readily dissolve. Another paper has in the meantime been placed in the funnel over the shaking-flask, and through this the material is filtered into the original solution. All operations, including the filtration of the residue, will not require 45 minutes; and the total solution and washings need not exceed 150 cc. Heat the combined filtrates to 90° C., add at once 75 cc. of molybdate solution (Reagent 6), causing mixture by whirling for a minute before placing the stopper in the flask. Shake violently for about five minutes, filter with the pump on a Munktell No. 0, 9 cm. paper, wash with 2%  $\text{H}_2\text{SO}_4$  (sp. gr. 1.84), and treat the yellow precipitate according to one of the methods previously given.

NOTE.—Of the various methods herein given for the determination of phosphorus, Mr. Wood's Direct Method, or some modification thereof, doubtless takes somewhat the least time, and, in the hands of a reasonably skillful chemist, is closely accurate. On account of its rapidity this method is given the preference above,

though there is little choice between it and the very fine method of Mr. J. O. Handy, referred to above.

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*Determination of Chromium.*—Fuse one gram of the ore with ten grams of  $\text{Na}_2\text{CO}_3$  and one gram of  $\text{KNO}_3$ . Cool, dissolve in water. If manganese is present, as indicated by the color, remove it by addition of  $\text{C}_2\text{H}_6\text{O}$ . If chromium is present the solution will be slightly yellow. Filter, wash, re-fuse the insoluble matter, take up in water, filter and unite the filtrates. Acidify with HCl and evaporate to dryness. Take up in HCl and water, filter and precipitate with  $\text{NH}_4\text{OH}$ , boil and filter, wash, dry and ignite the residue. Fuse with a very small amount of  $\text{Na}_2\text{CO}_3$  and  $\text{KNO}_3$ , take up with water and evaporate, in a platinum dish, till the solution is concentrated to small bulk, occasionally adding crystals of  $\text{NH}_4\text{NO}_3$ ; add a little  $\text{NH}_4\text{OH}$  and filter. To the filtrate add excess of  $\text{H}_2\text{SO}_3$  and boil; add excess of  $\text{NH}_4\text{OH}$  and boil; filter and wash with hot water. Dry, ignite and weigh as  $\text{Cr}_2\text{O}_3$ .

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*Determination of Alumina.*—Dissolve one gram of the ore in strong HCl; evaporate to dryness, moisten with HCl, take up with water and filter; dry and incinerate the residue, mix with  $\text{Na}_2\text{CO}_3$  and fuse, cool, dissolve with HCl and water and evaporate to dryness again; finally, take up in HCl and water and filter, adding the filtrate (if clear) to the main solution. The treatment of the residue with HF sometimes vitiates results, and cannot be recommended. Proceed from this point by Peters' modification of Wöhler's method, as follows:—Dilute to 400 or 500 cc. with cold water, and add  $\text{NH}_4\text{OH}$  until the solution becomes dark red in color, but

contains no precipitate. Now add 3.3 cc. of HCl, (sp. gr. 1.20), and two grams of sodium phosphate dissolved in water and filtered; stir until the precipitate formed is dissolved and the solution becomes perfectly clear again. Add 10 grams of sodium hypo-sulphite, dissolved in water and filtered if necessary, and 15 cc. of acetic acid, (sp. gr. 1.04), heat to boiling, boil fifteen minutes, filter as rapidly as possible on an ashless filter, wash thoroughly with hot water, dry, ignite in a porcelain crucible, and weigh as  $\text{AlPO}_4$ ; this weight, multiplied by 0.4185 gives the weight of  $\text{Al}_2\text{O}_3$ .

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*Determination of Arsenic, Antimony and Copper.*—Take a large sample (from 5 to 10 grams) of the finely pulverized and dried ore, and digest with HCl in an evaporating-dish, with occasional additions of small crystals of  $\text{KClO}_3$ , finally raising the heat to complete decomposition. Dilute with water, filter, reduce the ferric iron by boiling with addition of sulphurous acid or bi-sulphite of ammonium, and pass  $\text{H}_2\text{S}$  into the solution for 20 minutes. Allow the precipitate to subside, filter on asbestos, wash, transfer the residue to a beaker, and digest with potassium sulphide to dissolve antimony and arsenic; dilute with water, filter and wash, reserve filtrate, dissolve the residual sulphides in  $\text{HNO}_3$ , filter, wash, evaporate filtrate with addition of a few drops of  $\text{H}_2\text{SO}_4$ , take up with water and determine copper by the battery. (If lead is present, it will be separated as sulphate at this point). To the reserved filtrate add HCl to acid reaction, and digest at a gentle heat till sulphides of arsenic and antimony have settled; filter on asbestos filter, and wash with hot water. Treat the residue in an evaporating-dish, with HCl and  $\text{KClO}_3$ , warming gently, till it is completely dissolved, filter,

and wash. Concentrate the filtrate if necessary, add a small amount of tartaric acid, make alkaline with  $\text{NH}_4\text{OH}$ , then make thoroughly cold and add magnesia mixture, agitate briskly, and set aside for 10 hours. Filter, wash with ammoniacal water containing a little ammonium nitrate, dry, ignite, cool and weigh as magnesium pyro-arsenate. Make the filtrate containing the antimony slightly acid with HCl, dilute largely with water, heat gradually and pass  $\text{H}_2\text{S}$  into the solution : filter on a weighed filter, wash with water, then with alcohol and finally with carbon di-sulphide, dry at 100° C., and weigh; or the freshly precipitated sulphide of antimony can be examined according to the methods given under Analysis of Smelting Ores and Analysis of Zinc Ores.

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#### Complete Analysis of Iron Ores.

Place one gram of the prepared sample in a pint beaker, add 25 cc. of strong HCl and 2 cc. of strong  $\text{HNO}_3$ , evaporate to dryness and until the odor of HCl is completely expelled. Moisten again with HCl, and evaporate to dryness a second time. Cool, dissolve in 10 cc. of strong HCl and 15 cc. of water, filter, and wash five times with water. Dry the residue, and fuse it with 4 to 5 grams of  $\text{Na}_2\text{CO}_3$ , according to the amount of the residue. Pour the fusion into a nickel or platinum dish which is floating on water; place crucible cover and fused mass in a 6-inch porcelain dish, with 70 cc. of water and 30 cc. of HCl (sp. gr. 1.20); when dissolved; rinse cover and crucible, and evaporate to dryness and until HCl is expelled, cool, moisten with HCl and evaporate until HCl is again expelled. Cool, moisten with HCl and take up with water, filter and wash, dry, ignite and weigh as  $\text{SiO}_2$ .

Unite the filtrates, nearly neutralize with  $\text{NH}_4\text{OH}$ , then with  $\text{Na}_2\text{CO}_3$ , until the solution is dark-colored and cloudy, add ten drops of dilute HCl, boil for one-half minute, then add 10 cc. of a solution of ammonium acetate (two grams of the salt dissolved in 10 cc. of water), boil for two minutes and filter, using a 12 cm. ashless filter and a ribbed funnel. Wash four or five times with hot water, dissolve the precipitate with dilute HCl, and determine the alumina by the hypo-sulphite method as given above. Evaporate the filtrate to about 100 cc. in a 6-inch casserole, add 30 cc. of strong  $\text{HNO}_3$ , and heat; continue addition of  $\text{HNO}_3$  till the solution is colorless and no more red fumes are given off, thus decomposing ammonium chloride and acetate. Evaporate to moist dryness, leaving a faint excess of acid, dissolve in water, filter, wash five or six times, cool the solution, add bromine to brown color; warm to 80° or 90° C., add  $\text{NH}_4\text{OH}$  till bromine color disappears, and boil. Filter off manganese precipitate, wash on asbestos filter, and proceed by Method (4) for the determination of manganese, under Analysis of Iron and Steel. In the filtrate, precipitate the lime with ammonium oxalate, let stand over night, filter, wash, and determine the lime by the volumetric method given under Analysis of Limestone. To the filtrate add 10 cc. of  $\text{NH}_4\text{OH}$  and 15 cc. of  $\text{Na}_2\text{HPO}_4$ , let stand over night, filter, wash, and determine magnesia by weight of the pyro-phosphate. Determine the iron in a separate sample.

Converter, refinery and open-hearth slags, as well as mill and tap cinder, may be analyzed according to the methods given for iron ores.

### Analysis of Titanic Iron Ores.

Pulverize the ore very finely, dry, and place one gram in a beaker and mix with 10 cc. of water, until the ore is all in suspension. While shaking the breaker and contents, add 20 cc. of strong HCl and evaporate nearly to dryness on the water bath, stirring frequently. Add three drops of HNO<sub>3</sub> to oxidize the iron, and evaporate to dryness. Add 5 cc. of water and 20 cc. of H<sub>2</sub>SO<sub>4</sub> and evaporate on the water bath till SO<sub>3</sub> fumes arise. Cool thoroughly and mix with 50 cc. of water till everything is dissolved except the silica. Filter and reserve the filtrate.

*Res. (a).*—Ignite, cool, and weigh; treat twice with HF to remove silica, ignite, cool, and weigh again. The loss equals SiO<sub>2</sub>.

Thoroughly fuse the residue with KHSO<sub>4</sub>. Cool and treat with boiling water, when all should go into solution; add it to the reserved filtrate.

*Filt. (a).*—Dilute to 250 cc. with water, and take out four portions of 50 cc. each. Place one of these portions in each of two flasks, dilute with water to 100 cc., add 10 cc. of HCl and 10 cc. of a ten per cent. solution of KI. Loosely cork the flasks and warm them in water, at about 30° C., for twenty minutes. Make thoroughly cold and dilute to 250 cc. Titrate with n/40 thio-sulphate till the iodine color is nearly gone, add four drops of starch solution and titrate till the blue color is gone. The n/40 factor for Fe<sub>2</sub>O<sub>3</sub> is 0.0019975.

Add to each of the remaining 50 cc. portions 10 cc. of HCl and 5 grams of zinc and boil till the zinc is nearly dissolved. Make thoroughly cold, filter through glass wool, wash with cold water, add 50 cc. of a thirty per cent. solution

of  $MgSO_4$ , and titrate with n/40  $KMnO_4$ , for both iron and titanium.

Subtracting the iron found in the titration with thio-sulphate the remainder is  $TiO_2$ , for which the n/40 factor is 0.0020025.

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### Analysis of Chromic Iron Ores.

Carefully fuse 1 gram of the finely pulverized and dried ore in a large platinum crucible, with  $KHSO_4$ , for about ten minutes, or to thorough decomposition. Allow to cool slowly, and when cold, dissolve the fused mass in boiling water, with stirring. Add 15 cc. of strong  $H_2SO_4$  and heat to solution, filter and reserve the filtrate. Ignite, cool and weigh the residue, and treat with HF; ignite, cool and weigh. The loss equals the  $SiO_2$ . Fuse this residue with  $KHSO_4$ , cool and boil with water to solution; add the solution to the reserved filtrate. Cool and dilute to 500 cc.

Take 100 cc., add a slight excess of  $NH_4OH$ , boil, filter and wash with hot water. Dissolve the precipitate on the filter with hot dilute HCl, and re-precipitate with  $NH_4OH$ ; boil, filter and wash with hot water. Dry, ignite, cool, and weigh as  $Fe_2O_3$ ,  $Al_2O_3$ ,  $Cr_2O_3$ ,  $P_2O_5$ , etc.

Unite the two filtrates, boil and add a water solution containing 2 grams of  $(NH_4)_2C_2O_4$ , allow to evaporate very slowly down to 50 or 60 cc., filter and wash thoroughly with hot water. If the precipitate is large, dissolve it in HCl and re-precipitate with  $NH_4OH$ , filter, wash, dry, ignite and weigh as  $CaO$ .

Unite the two filtrates from the last operation and concentrate to 75 cc., make thoroughly cold, add excess of

$\text{NH}_4\text{OH}$  and  $\text{Na}_2\text{HPO}_4$ , and let stand from six to ten hours. Filter, wash with dilute  $\text{NH}_4\text{OH}$ , dissolve on the filter in a little dilute HCl, add excess of  $\text{NH}_4\text{OH}$ , make thoroughly cold and re-precipitate; filter in four hours, wash and ignite to  $\text{Mg}_2\text{P}_2\text{O}_7$ .

*For Chromium.*—Take 100 cc., evaporate one-half, occasionally adding a few crystals of  $\text{KMnO}_4$  during the boiling, until the pink color remains for a minute or two; then boil till all the  $\text{KMnO}_4$  is reduced to  $\text{MnO}_2$ , when the chromium will be oxidized to  $\text{Cr}_2\text{O}_3$ . Make thoroughly cold, filter, add a measured excess of standard  $\text{FeSO}_4$  (See Titration of Permanganate (a)) and titrate the excess of iron with n/10  $\text{KMnO}_4$ . n/10 factor for  $\text{Cr}_2\text{O}_3$  equals 0.0025366.

*For Iron.*—Place 100 cc. in a flask, add 15 cc. of HCl and five grams of granulated zinc of known reducing power, boil till the zinc is nearly dissolved. Make thoroughly cold, filter rapidly through glass wool, dilute to 300 cc., add 50 cc. of thirty per cent. solution of  $\text{MgSO}_4$  and titrate with n/40  $\text{KMnO}_4$ .

If the sample of chromite is not completely decomposed by the above method of fusion, it may be readily accomplished by following the directions given for the fusion of ferro-tungsten with sodium peroxide, under Analysis of Iron and Steel.

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### Analysis of Manganese Ores.

In the case of the mineral pyrolusite, it is usually valued in commerce according to the quantity of those oxides of manganese which will liberate chlorine. The moisture is determined by drying a crushed sample of the ore at  $120^\circ\text{C}$ . to constant weight. The dried sample is then placed in tightly stoppered bottles, before cooling, to be kept for analysis. Bunsen's method for determining the value of those oxides is based upon the following equation:  $\text{MnO}_2 +$

$4 \text{HCl} = \text{MnCl}_2 + 2 \text{Cl} + 2 \text{H}_2\text{O}$ . To apply this reaction, a weighed quantity of the sample of ore may be placed in a flask which is provided with a thistle-tube and also an exit-tube, the latter leading into a tube containing a solution of potassium iodide. Through the thistle-tube, HCl is gradually admitted to the ore, and the liberated chlorine reacts upon the potassium iodide. Warm the generating flask until solution is complete, remove the tube containing the potassium iodide and free iodine, and determine the latter by titration with standard sodium thio-sulphate; two atoms of iodine being equivalent to one molecule of manganese di-oxide.

The ordinary requirements in the analysis of manganese ores consist in the determination of silica, iron, manganese and phosphorus; a method for which is as follows:

*Portion for  $\text{SiO}_2$ , Fe and Mn.*—Take one gram of the ore, previously pulverized and dried at  $100^\circ \text{C}$ ., dissolve in HCl and evaporate to dryness; moisten with HCl, take up in water and evaporate again to dryness; moisten with HCl, take up in water and filter.

*Filtrate (a).*—Set aside.

*Residue (a).*—Dry, incinerate and fuse with  $\text{Na}_2\text{CO}_3$ ; take up in very dilute HCl, evaporate to dryness, take up again, and again evaporate to dryness. Take up with HCl and water and filter.

*Filtrate (b).*—Set aside to treat for the *insoluble* Fe and Mn.

*Residue (b).*—Dry, ignite and weigh as  $\text{SiO}_2$ . Nearly neutralize filtrate (a) with  $\text{Na}_2\text{CO}_3$ , add a water solution of 8 grams of  $\text{NaC}_2\text{H}_3\text{O}_2$ , heat *nearly* to boiling and keep at that temperature for two hours, filter and wash.

*Filtrate (c).*—Set aside. It should be colorless and clear.

*Precip. (c).*—Dissolve on the filter with hot, dilute HCl and re-precipitate with a slight excess of  $\text{NH}_4\text{OH}$ ; boil off the excess of  $\text{NH}_4\text{OH}$ , filter and wash.

*Filtrate (d).*—Set aside.

*Precip. (d).*—Place with the paper in a beaker and dis-

solve in HCl. Filter into a flask, washing thoroughly, add 5 grams of zinc and heat till the iron is reduced. Cool, filter through glass wool, add 10 cc. of H<sub>2</sub>SO<sub>4</sub> and 50 cc. of a thirty per cent. solution of MgSO<sub>4</sub>, make perfectly cold and titrate with n/40 KMnO<sub>4</sub> for Fe.

Unite filtrates (c) and (d), dilute to exactly 250 cc. and mix. Take a measured portion of from 25 to 50 cc., add a few drops of bromine, make alkaline with NH<sub>4</sub>OH, heat almost to boiling and shake.

Let stand at this temperature for one-half hour, filter and wash, testing the filtrate with bromine for manganese.

*Filtrate (e).*—If it contains no manganese, throw away.

*Precip. (e).*—Place with the paper in a beaker and dissolve the MnO<sub>2</sub> in a little strong HCl with heat. Filter and wash. Add to the filtrate 25 to 50 cc. of Na<sub>2</sub>HPO<sub>4</sub> (reagent), then add NH<sub>4</sub>OH, drop by drop, with constant stirring, until the solution is alkaline. Add a slight excess of NH<sub>4</sub>OH, let stand one-half hour, filter, wash with very dilute NH<sub>4</sub>OH, dry, ignite and weigh as Mn<sub>2</sub>P<sub>2</sub>O<sub>7</sub>.

Treat filtrate (b) for Fe and Mn, in a similar manner to filtrate (a).

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*Portion for Phosphorus.*—Dissolve two grams of the ore in HCl as before, evaporate twice to dryness, filter and wash.

*Residue (f).*—Set aside to determine *insoluble phosphorus*.

*Filtrate (f).*—Evaporate to 15 or 20 cc., add 25 cc. of HNO<sub>3</sub> and evaporate to 2 or 3 cc. Dilute slightly with water, add excess of NH<sub>4</sub>OH, and re-dissolve in HNO<sub>3</sub>. If the precipitate does not dissolve perfectly, add a few drops of HCl, heat to a clear solution, and again precipitate with

$\text{NH}_4\text{OH}$  and re-dissolve in  $\text{HNO}_3$ . Precipitate with molybdate solution (Reagent 6) and determine phosphorus as usual. Fuse residue (f) with  $\text{Na}_2\text{CO}_3$ , take up in HCl and water, evaporate twice to dryness and filter. Treat the filtrate for phosphorus as above. The residue may be weighed as silica.

If manganese alone is to be determined, dissolve one gram of the ore in HCl with addition of 5 to 10 cc. of  $\text{H}_2\text{SO}_4$ , and evaporate till  $\text{SO}_2$  fumes come off freely. Take up in boiling water and proceed by Volhard's method, as given under Analysis of Iron and Steel.

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### Analysis of Pig Iron.

*Determination of Silicon. Method (1).*—Take 1.1755 grams (Blair's "quarter factor weight"), dissolve in 25 cc. of Silicon Mixture (Reagent 15), evaporate rapidly till there is no danger of spattering, then more slowly, until dry and  $\text{SO}_2$  fumes come off. Cool, dissolve in dilute HCl with the aid of heat, filter, wash with hot dilute HCl, then with water; dry, ignite till all of the carbon is burned off and the residue is white, and weigh. The resulting silica, in milligrams, is multiplied by forty, and this result equals the per cent. of silicon.

*Method (2). Chromic Acid Modification of Drown's Method.*—To one gram of pig iron in a No. 5 evaporating dish, add 15 or 20 cc. of water and 25 cc. of Silicon Mixture (Reagent 15); heat gently till dissolved or till violent action ceases (the dish being covered with a clock-glass), and evaporate rapidly till the solution sputters. Remove the lamp and, while hot, add 15 cc. of a water solution of

chromic acid and boil again till the chromic acid crystallizes out. Dissolve by slow additions of hot water with boiling, filter and wash with hot water to remove chromic acid. Wash once with HCl (sp. gr. 1.06) and four times with hot water, dry, ignite and weigh. The use of chromic acid secures the combustion of the graphite in shorter time than it could be performed by ignition in the crucible.

NOTE.—Time required, 20 to 30 minutes Too long evaporation of the chromic acid solution causes formation of insoluble salts. A small amount of graphite remaining unoxidized is burned off on ignition. For shotted samples of pig iron, where less graphite is present, 8 cc. of chromic acid are sufficient

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*\*Determination of Phosphorus.*

NOTE.—It is difficult to completely oxidize all of the phosphorus in pig iron.

Dissolve 1.63 grams in 20 cc. of  $\text{HNO}_3$ , add excess of HCl (sp. gr. 1.20) and evaporate to dryness; bake for twenty minutes. If arsenic is present it will sometimes interfere with the determination; it may be eliminated at this point by re-dissolving in strong HCl, adding one gram of  $\text{H}_2\text{C}_2\text{O}_4$ , heating for ten minutes, and evaporating to dryness. Take up in strong HCl and 5 cc. of water, boil, filter and wash. Concentrate to 15 cc., add 25 cc. of  $\text{HNO}_3$  (sp. gr. 1.40) and evaporate to about 10 cc., cool, add 20 cc. of water, precipitate with  $\text{NH}_4\text{OH}$ , and re-dissolve in slight excess of strong  $\text{HNO}_3$ . Add about 50 cc. of molybdate solution (Reagent 6) cork tightly, cover with a cloth and shake; let stand one hour at 60° C., filter through a weighed

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\*See volumetric methods for phosphorus in pig iron under Analysis of Iron and Steel, also Phosphorus in Iron Ores and Products.

asbestos filter (See Rapid Analysis of Pig Iron), wash thoroughly with 2%  $\text{HNO}_3$ , dry one hour at  $125^\circ \text{C}.$ , cool and weigh. Each milligram equals 0.001 per cent. phosphorus.

The yellow precipitate obtained as above, may also be treated by the methods given under Analysis of Iron and Steel, or by the magnesia method, as given under Phosphorus in Iron Ores and Products.

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*Determination of Sulphur.*—See Methods 1, 2, 3, and 4 under the head of Analysis of Iron and Steel.

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*Determination of Manganese.*—See Analysis of Iron and Steel, also Rapid Analysis of Pig Iron.

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*Determination of Carbon.*—(Mr. Textor's method for Graphite). Carefully weigh two grams of the pig iron (being careful to use a non-magnetic spatula) and place in a No. 3 beaker, add 40 cc. of  $\text{HNO}_3$  (sp. gr. 1.20) and 75 cc. of water. Keep near, or at, the boiling point for 30 minutes, add 15 cc. of strong  $\text{HCl}$  and heat for another 15 minutes; add 5 cc. of  $\text{HF}$ , heat five minutes and filter through a weighed filter; wash with water containing 2% of  $\text{HNO}_3$  (sp. gr. 1.20) from ten to twelve times, finishing with two or three washings with distilled water, dry and weigh as directed for the yellow precipitate under the direct method for determination of phosphorus. After weighing, ignite the filter and residue, cool, weigh and deduct ash if any. See also Graphite under Rapid Analysis of Pig Iron, and Total Carbon under Analysis of Iron and Steel.

*Combined Carbon.*—(Mr. Textor's Method.) Dissolve 0.200 grams of the pig iron in 3 cc. of HNO<sub>3</sub> (sp. gr. 1.20); if color indicates over 0.20 carbon, use 3.5 or 4 cc. of HNO<sub>3</sub>, instead of 3 cc. Use a .12, .15, .25 or .40 carbon standard, as the condition may require; dissolve in the same manner as with the sample, by heating at 95° to 98° C. for 10 or 12 minutes, cool. Dilute solution of pig iron to definite mark, mix in dilution tube and filter. Now dilute the standard to the proper mark (i. e., 2 cc. for each 0.1 C.), mix and filter (in order to obtain similar conditions as with pig solution). Now dilute the solution of the pig iron to the color of the standard, and calculate as follows:—If, before filtering, the pig iron solution is diluted to 4 cc., and if 3 cc. of this solution is taken for dilution and comparison and if this 3 cc. has been diluted to 4 cc., then 3:4::4:5.3; divide .53 by 2, and we obtain .26 for the combined carbon in the sample of pig.

*Determination of Aluminum, Chromium and Titanium.*—See Analysis of Iron and Steel.

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#### Rapid Analysis of Pig Iron.

*Sampling.*—Five or six pigs may be selected, at random from a carload, broken and drilled in the following manner; one piece is drilled near the top, the next piece near the center, the next near the bottom and so on, carefully collecting the drillings, as they are produced, and mixing them thoroughly.

*Preparation of Apparatus.*—A small, one-inch, funnel is heated at the lower end, and drawn out to a small point, so that the opening may be one-fourth its former diameter. A

small plug of glass wool is placed in the neck, the funnel is then connected with the filter pump and asbestos suspended in water is poured into it, this is drawn down by the suction and more is added, until the different layers of asbestos fill the funnel to within one-quarter inch of the top. The asbestos should be previously digested in hot HCl, for 12 hours, carefully washed, dried and ignited. (The use of this appliance for filtering was suggested by Professor Campbell.) Several of these filters should be kept ready for use.

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*Determination of Graphite.*—Dissolve one gram of the drillings, in a beaker, in a mixture of 10 cc. strong HNO<sub>3</sub> and 18 cc. H<sub>2</sub>O. Heat to boiling until all action ceases, wash down the sides of the beaker, diluting to about 50 cc., stir and allow to stand a few minutes in cold water until settled.

Fit a two-holed rubber stopper in the neck of a 100 cc. graduated flask, adjust one of the prepared funnels, and connect apparatus with the filter pump. Filter the contents of the beaker and wash several times. If filtration is slow, on account of gelatinous silica, add a drop or two of HF to the contents of the beaker. Remove the funnel, place it in another flask in connection with pump, and wash, first with hot solution of KOH, then with hot water, then with hot dilute HCl, and finally with hot water. With a pair of forceps peel off the upper layer of asbestos, which carries most of the graphite, and place it in a platinum crucible, then peel off successive layers holding them in the forceps, and wiping out the funnel with them, until all the graphite has been removed and transferred to the crucible. Dry the crucible and contents at 100° C., cool and weigh; ignite until all of the

graphite is burned, and weigh again. Loss of weight is graphite.

**Note**—This method checks well with results made by use of the combustion furnace

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*Determination of Combined Carbon.*—Return to the first filtrate, dilute to the mark, mix thoroughly and take 10 cc. with an accurately graduated pipette; place in a carbon color-tube (See Colorimetric Determination of Combined Carbon) and compare with 10 cc. of standard pig iron, dissolved at the same time as the sample and in the same manner.

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*Determination of Manganese.*—(*Method (1), Modification of Chatard's or Deshay's process.*)\* Take from 5 to 10 cc. of the solution, according to the amount of manganese suspected, place in a large test tube, add from 1 to 4 grams of  $\text{PbO}_2$  to oxidize all of the manganese and 5 cc. of strong  $\text{HNO}_3$ , boil three minutes, and stand in a beaker of cold water to settle. Filter by suction, through an asbestos filter, into another large test tube and wash with cold water. Rinse the filtrate into a beaker and titrate with a standard solution of  $\text{As}_2\text{O}_3$ . The solution of  $\text{As}_2\text{O}_3$  is standardized against a steel or pig iron whose manganese content is known, and should be of such strength that 1 cc. equals 0.0001 grams of manganese.

*Method (2).*—(*Colorimetric modification of the above process, by H. E. Walters.*) In examination of a steel, if the manganese content is 0.75% or higher, take 0.100 grams; if less than that amount, take 0.200 grams. The requisite

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\*Bull. Soc. Chem. de Paris, June 20, 1878.

weight of the steel and a similar weight of a standard steel of known manganese content, are placed in test-tubes; 10 cc. of  $\text{HNO}_3$  (sp. gr. 1.20) are added to each, and the tubes placed in a water-bath till nitrous fumes no longer appear. Add 15 cc. of a solution of  $\text{AgNO}_3$  (1.33 grams per litre), thus cooling the solutions; now add about one gram of ammonium per-sulphate salt to each, and warm till oxidation commences, and about a half minute longer. Remove the tubes from the baths while the evolution of oxygen continues, and place in a cold water bath. When the solutions are cool, they are compared as usual. In case of pig iron, the solution of the sample is filtered, and the filter washed with the 15 cc. of silver solution.

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### Analysis of Iron and Steel.

*Determination of Sulphur. Method (1).*—Place five grams of drillings in an 8-oz. flask, provided with a thistle tube and connected with one 8-inch, plain U-tube. Place 25 cc. of  $\text{ZnSO}_4$  solution (Reagent 21) in the U-tube, and add 75 to 85 cc. of dilute  $\text{HCl}$ , (one part acid to two parts of water) to the drillings. When about all of the drillings are dissolved, heat to boiling and continue till the arm of the U-tube nearer the flask becomes hot from the steam. Pour contents of U-tube into a beaker, and rinse U-tube with  $\text{HCl}$  and water sufficient to acidify the  $\text{ZnSO}_4$  solution; add rinsings to the solution in the beaker, and titrate with standard iodine (Reagent 23).

*NOTE.*—In the case of Pig Irons, where the material is treated with  $\text{HCl}$  and the sulphur determined in the liberated gases (as in this and the following methods), the sulphur remaining in the carbonaceous residue should always be determined. In some cases

the residue, after being filtered off and washed on an asbestos filter, may be treated with HCl and bromine; the solution then being diluted, filtered, and the sulphuric acid precipitated with barium chloride, with the usual precautions. In general, however, it is better to pulverize the washed and dried residue, and fuse it with Reagent (1); the fusion is cooled, dissolved in hot water, filtered, the filtrate made acid with HCl, then evaporated to dryness, taken up with hot water, acidified with HCl, filtered, and the filtrate treated with barium chloride as usual.

*Method (2).*—Take from three to five grams, place in a generating flask which has a funnel tube with a stop-cock, connect the flask with three small, three-bulb U-tubes; fill these tubes one-third full with a solution of KMnO<sub>4</sub> (one gram KMnO<sub>4</sub> to 200 cc. of water). KMnO<sub>4</sub> must be free from sulphuric acid. Now, gradually let into the generating flask dilute HCl (one part HCl to two parts of water). The HCl must be free from chlorine. A rapid evolution of gas must be avoided. Continue the operation until all of the iron is dissolved, then heat the flask nearly to boiling, and draw air through for some time. Empty the U-tubes into a beaker, rinse first with water, then with strong HCl to dissolve the oxide of manganese adhering to the sides. Now add about 15 cc. of strong HCl and evaporate rapidly; after the solution has been reduced to about one-half of its original bulk, if it is not clear, add more HCl and continue the boiling until a clear solution is obtained; that is, until the KMnO<sub>4</sub> has all been reduced. Neutralize the excess of HCl with ammonia and precipitate the sulphuric acid in the usual manner. If this last solution contains a sediment on account of impurities in the KMnO<sub>4</sub>, filter before precipitation.

*Method (3).*—Proceed according to directions given in Method (2), using in the U-tubes, in place of KMnO<sub>4</sub>, a solution of caustic soda (one part NaOH to five parts of

water). This solution of soda must be free from sulphur, or its compounds, or any agent which will affect iodine. Empty the U-tubes into a large flask, rinse well with water, and dilute to 200 or 300 cc., acidify with strong HCl (free from chlorine), add starch solution, and titrate with n/100 solution of iodine.

The n/100 factor for sulphur equals 0.0001603.

*Method (4).*—Take 15 cc. of the CdCl<sub>2</sub> solution (Reagent 26), dilute it with 150 cc. of water; if a precipitate forms add some NH<sub>4</sub>OH to dissolve it. Now take five grams of iron in a generating flask and dissolve it with dilute HCl (one part of acid to two parts of water) and pass the gas into this last solution of CdCl<sub>2</sub>. When the iron is all dissolved, dilute the cadmium solution with water to 400 cc.; then add, gradually, dilute HCl till the solution is acid; now titrate with standard iodine.

If perfectly accurate results are desired the cadmium sulphide must be filtered off and then removed from the filter and titrated; for the cadmium solution which destroys iodine, absorbs carburetted-hydrogen, thus giving too high a per cent. of sulphur.

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### *Volumetric Determination of Phosphorus.*

The methods given for the determination of phosphorus which are dependent upon (1) the direct weight of the dried yellow precipitate,\* or (2) the volumetric treatment of this precipitate,† are based upon the hypothesis that the yellow precipitate of phosphomolybdate of ammonia is of constant composition. Although this is probably true for this salt, if precipitated and dried under constant conditions, it is also true that its composition has been found to vary

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\*See Wood's Direct Method, under Analysis of Iron Ores, also under Analysis of Pig Iron.

†See the methods of Handy and Emmerton, below.

widely under slightly differing conditions; with the result that it has been known to contain from 1.17%<sup>k</sup> to 1.91%<sup>†</sup> of phosphorus, with, of course, a corresponding variation in the percentages of molybdic acid. It should then be noted, that the safe procedure in using these methods requires a strict conformance with the prescribed manipulations for the size and character of solutions, the temperature of precipitation, the size and character of wash solutions, the temperature at which the yellow precipitate is dried, and the time of drying. With a reasonable regard for these conditions, these methods will be found very accurate indeed, and of great value as time-savers. Where the chemist is required to make frequent phosphorus determinations, it will be found advisable to make a number of phospho-molybdate precipitations, carefully observing the conditions, and finally determining the phosphorus by the magnesia precipitation method, as given under Phosphorus in Iron Ores and Products. He should also make another set of precipitations, carefully observing the conditions and carefully drying the precipitates for one hour at 125° or 135°C.; afterward dissolving and determining the phosphorus by the magnesia method. This procedure will enable him to establish his own percentage figures, in the first case, for use in the volumetric method; in the second case, for use in the direct weighing of the yellow precipitate.

*Method (1), by Mr. J. O. Handy.*—Dissolve two grams of steel in a 12-oz. Erlenmeyer flask, in 75 cc. of HNO<sub>3</sub> (sp. gr. 1.13); to the boiling solution add 15 cc. KMnO<sub>4</sub> solution (five grams per litre) and boil until the pink color disappears. Oxidation of the carbon and phosphorus is complete if there remains a brown precipitate of MnO<sub>2</sub>, and more permanganate will be required only in the analysis of iron and steel of very high carbon. Remove the flask from heat and add 1/30th gram of granulated sugar; replace flask upon heater and heat till solution clears. Remove flask and after two or three minutes add 13 cc. of 90 per cent. NH<sub>4</sub>OH, pouring carefully down the side of the flask to prevent spattering; agitate the flask till, in a moment, the ferric hydrate

\*Sonnenschein, *Journ. f. prakt. Chem.*, LIII., 342.

†Eggertz., *Ibid.* LXXXIX., 496

is dissolved. Insert thermometer and warm (or cool) to 85° C., add 50 cc., molybdate solution (Reagent 6), causing it to rinse off thermometer. Insert rubber stopper, wrap flask in cloth, or put into a shaking box, and shake five minutes. Filter immediately, using a 9 cm. Swedish filter, and moderate suction. Wash out flask and wash filter and contents five times with one per cent. HNO<sub>3</sub>, and five times with 1/10th per cent. KNO<sub>3</sub>. Place filter and contents in the flask, add, from a pipette, 10 or 20 cc. of the standard NaOH solution (Reagent 7-b). Shake for a minute until the yellow precipitate is dissolved. Dilute with water to about 50 cc., add three drops of phenol-phthalein indicator, and titrate with standard HNO<sub>3</sub> (Reagent 7-c) till the pink color disappears. Each cc. of standard NaOH used represents 0.01 per cent. of phosphorus in the sample.

*Remarks.*—Mr. Handy states that 0.014 per cent of arsenic in steel needs no consideration when the phosphorus is determined by the above method; also that there is perfect agreement between results obtained by weighing and titrating the yellow precipitate, it having been dried at 100° C. to 150° C. before weighing, and figured at 1.63 per cent. phosphorus.

NOTE I.—To adapt this valuable method to the determination of phosphorus in pig iron, all that is necessary, after solution as with steel, is to filter off the graphite.

NOTE II.—Mr. Handy's process for iron ores, free from titanic acid, is as follows: Dissolve in HCl, with enough HNO<sub>3</sub> to oxidize FeO, and evaporate to dryness; re-dissolve in HCl, dilute and filter into an Erlenmeyer flask. Ignite residue and filter, treat with a few drops of H<sub>2</sub>SO<sub>4</sub> and about 5 cc. of HF. The silica is expelled by evaporation and the residue ignited, fused with Na<sub>2</sub>CO<sub>3</sub> and a little KNO<sub>3</sub> and boiled to solution with water. The crucible is removed, the solution acidified with HCl, boiled and added to the main HCl solution. Ammonia is added until the solution smells of it; after shaking, add strong HNO<sub>3</sub> till the precipitate is re-dissolved and the solution is a light brown color. Heat to 85° C. and precipitate as usual.

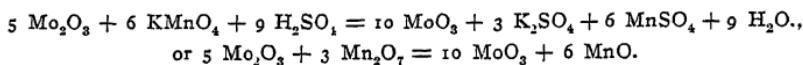
NOTE III.—To adapt the process to Chilled Iron and Ferro-Man-

ganese it is necessary to dissolve the sample in HNO<sub>3</sub>, either concentrated or dilute, and evaporate to hard dryness; re-dissolve in HCl and proceed as in the case of iron ores, in Note II above

*Method (2), by Mr. F. A. Emmerton.\**

This volumetric method is based upon the fact that the MoO<sub>3</sub> in the phospho-molybdate precipitate can be reduced to Mo<sub>2</sub>O<sub>5</sub> by use of zinc and dilute H<sub>2</sub>SO<sub>4</sub>, and the Mo<sub>2</sub>O<sub>5</sub> thus formed can be oxidized to MoO<sub>3</sub> by titration with permanganate.

The reaction with permanganate is as follows:



Examining the above reaction, we find that six parts of permanganate oxidize ten parts of molybdenum. A standard solution of permanganate is desired, each cc. of which shall react with an amount of the yellow precipitate containing 0.0001 grams of phosphorus. If the yellow precipitate contains 1.794% of phosphorus,  $0.0001 \div 0.01794 = 0.005574$ , which is the weight of yellow precipitate which will contain 0.0001 grams of phosphorus. If the yellow precipitate contains 61.113% of molybdenum, 0.005574 grams will contain 0.003406 grams of molybdenum. If (by inspection of the equation) the ratio between permanganate and molybdenum may be expressed as 31.63 : 32 (reduced from 948.9 : 960), we have  $31.63 : 32 :: x : 0.003406$ ; from which  $x$  equals the necessary weight of permanganate in 1 cc. of the standard solution, which shall be equivalent to 0.0001 grams of phosphorus; or,  $x$  equals 0.00336661 grams. The solution of permanganate should then contain 3.3666 grams per litre.

For steel, dissolve 5 grams in 75 cc. of HNO<sub>3</sub> (sp. gr. 1.20) in a dish covered by a watch glass. Boil to dryness and heat 30 minutes. Cool, add 40 cc. of strong HCl, cover tightly and dissolve with gentle heat; boil down to 15 cc. Cool, add 40 cc. of strong HNO<sub>3</sub> and boil down to 15 cc. Dilute to about 40 cc. and wash into a 400 cc. flask, bringing the solution up to about 75 cc.; add strong NH<sub>4</sub>OH, shaking after each addition till the mass is thick and there is a strong smell

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\*Pisani's method.

of  $\text{NH}_4\text{OH}$ . Dissolve in strong  $\text{HNO}_3$  and add enough to make the solution a clear amber color. Heat or cool to 85° C., cork the flask after adding 40 cc. of molybdate solution (Reagent 6-b), cover with a cloth, shake violently for five minutes, and filter.

Use the filter pump in washing, and wash the yellow precipitate thoroughly with two per cent.  $\text{HNO}_3$ . Place about ten grams of granulated zinc in a 500 cc. flask, place the funnel containing the moist precipitate in the neck of the flask, punch a hole in the filter and wash the precipitate into the flask with dilute  $\text{NH}_4\text{OH}$ . Pour into the flask 80 cc. of hot, dilute  $\text{H}_2\text{SO}_4$  and cover the neck with a small funnel. Heat rapidly till the zinc begins to dissolve and then gently for ten minutes. Pour the reduced solution onto a large ribbed filter, rinse out the flask with cold water and pour these washings on the filter, fill the filter once with cold water. Titrate the cold solution with n/10  $\text{KMnO}_4$ .

NOTE I.—For Pig Irons the  $\text{HNO}_3$  solution, made as before, is filtered and four-fifths of the filtrate taken for determination of the phosphorus, thus keeping the bulk of the solution constant.

NOTE II.—For Iron Ores, 10 grams are taken, dissolved in  $\text{HCl}$ , evaporated to dryness, taken up in  $\text{HCl}$ , and the  $\text{HCl}$  expelled by boiling down with 40 cc. of strong  $\text{HNO}_3$ . The insoluble residue is filtered off and the process continued as before.

NOTE III.—The reducing action upon the  $\text{KMnO}_4$  of the zinc used should be accurately titrated, and a correction factor determined therefor.

For gravimetric method, see Phosphorus in Iron Ores and Products.

*Determination of Manganese. Method (1).—Volumetric method, as modified by Mr. J. V. R. Stetman\**). Weigh 0.200 grams of the sample of iron or steel, and place in a 6-inch test tube; add 10 cc. of  $\text{HNO}_3$  (sp. gr. 1.20), heat to boiling in hot water bath till dissolved and free from nitrous fumes. In the case of pig iron, this solution must be freed from graphite by filtration. Filter into a 10 by 1-inch test-tube (using a small filter), wash filter twice with hot water containing a little  $\text{HNO}_3$ , and add through the filter to the contents of the tube, 15 cc. of a solution of silver nitrate (1.33 grams to the litre). Now add 1 gram of ammonium per-sulphate and boil, heating for about one minute after oxidation begins. Cool the tube and contents rapidly, under the spigot, and pour into a No. 2 beaker, washing out the tube with 30 or 40 cc. of water; if the presence of silver salts interferes in the titration, they may be removed at this point by addition of 5 cc. of a saturated solution of sodium chloride. Titrate with a solution of sodium arsenite which has been standardized against permanganate or an iron in which the manganese has been accurately determined.

NOTE.—See colorimetric modification of this method under Rapid Analysis of Pig Iron.

*Method (2), Volhard's Method.*—Take of steel 2 grams, of spiegel or ferro-manganese 0.500 grams if very high in manganese or 1 gram if containing less than 40 per cent., of pig iron 2 grams. Dissolve the sample in  $\text{HNO}_3$  (sp. gr. 1.20) in a No. 2 beaker and boil down to 10 cc.; introduce into a 500 cc. flask, and precipitate with emulsion of  $\text{ZnO}$  (Reagent 16) using an excess. Dilute to the mark with

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\*Journal Am. Chem. Society, XXIV. p. 1204.

water and mix thoroughly. Allow to settle and draw off a convenient portion, 100 to 200 cc., transfer to another flask and boil. At this point add, for ferro or spiegel, 3 drops of  $\text{HNO}_3$  (sp. gr. 1.20). Titrate with standard  $\text{KMnO}_4$ , boiling between additions, until a permanent pink tinge remains. The n/10 factor for manganese is 0.00165.

*Method (3).*—Take of the metal such weight as advised under Method (1), and dissolve it in strong  $\text{HNO}_3$ . In the case of pig iron, filter off graphite through an asbestos filter. Evaporate to a pasty condition, add 40 cc. of strong  $\text{HNO}_3$  and boil, with occasional additions of pulverized  $\text{KClO}_3$  until about two grams have been added. Add 20 cc. of strong  $\text{HNO}_3$  and another pinch of  $\text{KClO}_3$ , boil five minutes, cool, filter through an asbestos filter (See Rapid Analysis of Pig Iron) and wash with pure, strong  $\text{HNO}_3$  by suction.

(X) Dissolve the  $\text{MnO}_2$  on the filter with dilute  $\text{H}_2\text{SO}_4$  (made by adding a slight excess of  $\text{HCl}$  to  $\text{NH}_4\text{HSO}_4$ ), using a slight suction at first. Boil the filtrate to drive off  $\text{SO}_2$ , add 3 cc. of  $\text{HNO}_3$  and boil. Precipitate the iron by addition of a solution of two grams of  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ , filter and wash, re-dissolve the precipitate in  $\text{HCl}$ , re-precipitate the iron, filter and unite the filtrates. Heat nearly to boiling, add solution of ammonium phosphate and a slight excess of  $\text{NH}_4\text{OH}$  and boil. Filter, wash, dry, ignite and weigh as  $\text{Mn}_2\text{P}_2\text{O}_7$ , of which 38.732 per cent. is manganese.

*Method (4).—Williams' modification of Ford's method.*—Commencing at (X) in the method above, the  $\text{MnO}_2$  precipitate is thoroughly washed with water, the layer of asbestos carrying the precipitate is removed and placed in a beaker; to this is added a measured excess of a standard solution of oxalic acid and water, to bring the volume up to

75 cc. Add 3 cc. of strong  $H_2SO_4$  and heat to about  $70^{\circ} C.$  with stirring. Titrate the excess of oxalic acid with standard  $KMnO_4$ .

See also the methods given under Rapid Analysis of Pig Iron.

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*Determination of Silicon.*—Dissolve 5 grams of steel in 100 cc. of Silicon Mixture (Reagent 15) and evaporate till  $SO_3$  fumes arise. Add from 5 to 10 cc. of strong HCl and 15 cc. of water and boil until dissolved. Filter and wash thoroughly, dry, ignite and weigh.

In Spiegeleisen and Ferro-manganese the silicon is usually low and may be determined as in Pig Iron or Steel. Phosphorus may also be determined as in Pig Iron or Steel.

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*Determination of Aluminum. Method (1).*—Dissolve 10 grams of the sample in a 500 cc. flask (which is closed with a stopper carrying a rubber valve to prevent oxidation of the iron), in 130 cc. of one-fourth strength HCl, heating on the water bath to complete solution. For steel, no filtration is necessary, but in case of pig iron, filter through a ribbed filter into a flask of similar capacity, into which has been placed 3 grams of  $NaHCO_3$ , and wash the residue. To the filtrate add  $NH_4OH$  almost to precipitation, and heat nearly to boiling. Add gradually, until the yellow color is gone, a solution made of equal parts of  $NH_4OH$ ,  $NH_4HSO_3$  and water, shaking after each addition. If the ferrous precipitate fails to re-dissolve, add barely enough HCl to cause its solution. When the iron is all reduced, as indicated by the disappearance of the yellow color, add 1 cc. of a 10 per

ent. solution of  $\text{Na}_2\text{HPO}_4$  and 30 cc. of  $\text{NaC}_2\text{H}_3\text{O}_2$  reagent, heat and filter off phosphates of iron and aluminum, using the filter pump. Wash carefully and dissolve in HCl on the filter. Evaporate the filtrate with addition of 2 cc. of  $\text{H}_2\text{SO}_4$ , till  $\text{SO}_3$  fumes arise. Take up in water, wash this through filter to remove any silica, dilute to 125 cc., add  $\text{Na}_2\text{HPO}_4$  s before and boil. While boiling gradually add a saturated solution of  $\text{Na}_2\text{S}_2\text{O}_3$  till all the aluminum is precipitated, filter, wash and dissolve on the filter in hot dilute HCl. If the solution is yellow, the iron has not all been removed. Add three drops of  $\text{HNO}_3$  and heat. Add 1 cc. of  $\text{Na}_2\text{HPO}_4$  solution and dilute to 60 cc., heat and add a slight excess of  $\text{NH}_4\text{OH}$ , boil, filter and wash thoroughly with hot water, dry and ignite to a dull red heat, cool and weigh as phosphate of aluminum, of which 22.194 per cent. is aluminum. If the weighed residue shows any color from the presence of iron it should be dissolved and the iron determined, then, figured as ferric phosphate, it should be subtracted from the weight of aluminum phosphate obtained.

\**Method (2).*—Treat 10 grams of the pig iron or steel, in platinum dish, which is covered with a piece of platinum foil, with hydrochloric acid; when solution is complete, dilute and filter into a flask, washing the carbon, silica, etc., on the filter, thoroughly, with distilled water. Neutralize the solution with ammonia and sodium carbonate, but see that no permanent precipitate is formed; add a little sodium thiosulphate and when the liquid (at first violet) becomes colorless, add 2 or 3 cc. of a saturated solution of sodium phosphate and 5 or 6 grams of sodium acetate dissolved in a little water. Boil the solution for about 15 minutes, or until

it no longer smells of sulphurous acid, filter and wash the precipitate (aluminum phosphate, mixed with a little silica and ferric phosphate) with boiling water. Treat the precipitate on the filter with hot, dilute HCl, allow the solution to run into a platinum dish, evaporate to dryness and heat for one hour at 100° C., to render silica insoluble. Dissolve in hot dilute HCl, filter off silica, dilute to 100 cc. with cold water, neutralize as before, add a little sodium thiosulphate in the cold, then add a mixture of 2 grams of sodium thio-sulphate and 2 grams of sodium acetate, boil until all smell of sulphurous acid has disappeared, filter, wash, dry, ignite and weigh as AlPO<sub>4</sub>.

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*Determination of Chromium.* *Method (1).*—Dissolve 5 grams of the metal in HNO<sub>3</sub> or aqua regia, evaporate to dryness and burn off carbonaceous residue. Fuse the residue with KHSO<sub>4</sub> and proceed as directed under Analysis of Chromic Iron Ores.

*Method (2).*\*—Weigh 2 grams of drillings, place in a flask which is closed with a stopper carrying a glass tube provided with a rubber valve (to prevent oxidation of iron), add a small piece of Na<sub>2</sub>CO<sub>3</sub> (about 0.500 grams) and 30 cc. of dilute HCl (15 cc. of HCl and 15 cc. of water), cork the flask and warm on the water-bath or hot-plate to solution. When dissolved, add some more Na<sub>2</sub>CO<sub>3</sub> and 75 cc. of cold water, and cool quickly. Add solid Na<sub>2</sub>CO<sub>3</sub> till almost neutral, then add an excess of precipitated BaCO<sub>3</sub> (Reagent 35) till the solution is quite milky, loosen the stopper, shake at intervals for several hours, and let stand three

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\*As modified from Blair.

hours well corked. Filter rapidly, wash with cold water, place a clean beaker under the funnel, pierce the filter and wash contents into the beaker. Wash the flask and filter with hot dilute HCl, then with hot water, and add washings to the contents of beaker. Dissolve the soluble contents of the beaker in HCl, with a few drops of HNO<sub>3</sub> to oxidize ferrous iron, boil and precipitate in the usual manner with NH<sub>4</sub>OH. Boil three or four minutes, or till the odor of ammonia is gone, allow to subside, filter and wash well with hot water; dry, separate the residue from filter as completely as possible, ignite filter and add to residue. Carefully pulverize this lumpy residue in an agate mortar. In a platinum crucible place 3 to 6 grams of Na<sub>2</sub>CO<sub>3</sub> and ½ gram of KNO<sub>3</sub> for steels (for pig irons, from 2 to 3 grams of KNO<sub>3</sub> are necessary), add residue, and mix thoroughly. Gradually heat to fusion, until KNO<sub>3</sub> is decomposed; cool, dissolve in hot water, filter and wash well with hot water, make acid with HCl and boil; add a little sodium sulphite, boil two or three minutes, and precipitate with NH<sub>4</sub>OH; finally boiling for a few minutes more. Filter, wash well, dissolve in HCl, evaporate to dryness to separate silica; cool, take up in HCl, dilute, filter off silica, and precipitate Cr<sub>2</sub>O<sub>3</sub> with NH<sub>4</sub>OH. Filter, wash well, dry, ignite and weigh. The precipitate may contain small amounts of alumina and phosphoric acid. Mr. Textor advises a second fusion of the oxides from the first precipitation with ammonia.

*Determination of Titanium.*

Steels rarely carry more than a trace of titanium, but notable quantities exist in some pig irons

Dissolve from 5 to 10 grams of the pig iron in Silicon Mixture (Reagent 15), and evaporate till fumes of  $\text{SO}_3$  come off in large quantity, using about 20 cc. of the mixture to each gram of the metal. Cool, take up in water and  $\text{HCl}$ , filter and wash, dry and ignite till all of the carbon is burned off. Add a few drops of water, three drops of  $\text{H}_2\text{SO}_4$  and HF according to the quantity of the residue. After violent action has ceased, evaporate to dryness. Fuse the residue with  $\text{Na}_2\text{CO}_3$ , take up in water and  $\text{H}_2\text{SO}_4$ , filter and wash, adding the filtrate to the former filtrate. Add 50 cc. of a strong solution of  $\text{H}_2\text{SO}_3$ , filter if necessary, add a clear filtered solution containing 20 grams of  $\text{NaC}_2\text{H}_3\text{O}_2$  and one-sixth the volume of the solution of acetic acid (sp. gr. 1.04), and boil for a few minutes. Allow the  $\text{TiO}_2$  to settle, filter, wash with hot water containing a little acetic acid, dry, ignite and weigh as  $\text{TiO}_2$ , of which 60.049 per cent. is titanium.

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*Determination of Total Carbon. (See illustration).—*

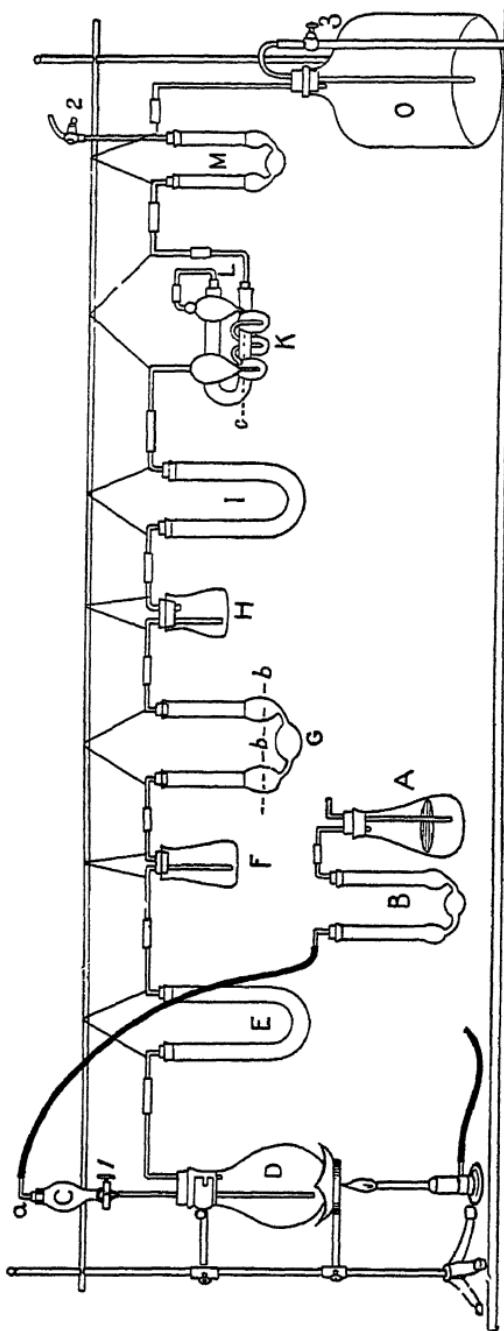
The summation of various investigations upon this subject, by Professor J. W. Langley,\* while considering the two methods of combustion, the wet and dry, shows no marked preference for either to the disadvantage of the other, and it is probable that, where preference exists among chemists, it is largely due to greater familiarity with the method preferred. Since the wet combustion requires simpler and less expensive apparatus, it is herein considered; both methods are exhaustively considered in Professor Langley's paper.

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\*Transactions, A. I. M. E., XIX, 614, XX, 242.

*Apparatus.*—The bottle A is filled one-third full of KOH solution; B is a soda-lime tube; their purpose is to prevent the entrance of CO<sub>2</sub> from the air. The funnel tube C transmits the oxidizing solution into the combustion flask D, and is connected with the tube B by a rubber tube; it is provided with a stop-cock. The tube E is filled with pumice stone and anhydrous sulphate of copper; F is a small bottle containing solution of pyro-gallic acid, whose purpose is to absorb chlorine compounds not taken up by copper or silver sulphates; G is a U-tube filled to the mark *b* with solution of Ag<sub>2</sub>SO<sub>4</sub>, to absorb chlorine; H is a small bottle containing strong H<sub>2</sub>SO<sub>4</sub>, to absorb moisture; I is a tube, filled with granular calcium chloride, provided with a plug of cotton in its anterior end; K is a potash bulb, filled to the mark *c*, with solution of KOH (sp. gr. 1.27); L is a plain 4-inch U-tube, connected with and fastened to the potash bulb K, whose upper arm is filled with soda-lime and whose lower arm is filled with granular calcium chloride; both K and L are for the absorption of the CO<sub>2</sub>; M is a guard tube, the right arm filled with soda-lime and the left arm filled with granular calcium chloride; O is an aspirator bottle of five litres capacity.

*Solution of the Iron and Steel.*—Weigh three grams of the pig or cast-iron, or five grams of steel or wrought iron, add 200 cc. of the solution of double chloride of potassium and copper (Reagent 24), stir frequently, and, after a few minutes, apply a gentle heat (50° to 60° C.), and add 7½ cc. of HCl for each gram of the sample taken. When the iron and precipitated copper are dissolved, filter through asbestos and wash three times with 5% HCl, then thoroughly with hot water, till the washings are free from chlorides.



APPARATUS FOR THE DETERMINATION OF CARBON WET COMBUSTION METHOD

*Combustion of the Carbon.*—Transfer the layer of asbestos containing the carbon to flask D, connect all the apparatus and aspirate one litre of air, valves (1) and (3) being open and valve (2) closed. Close valve (3) and open valve (2). Let apparatus stand in this condition fifteen minutes, disconnect K and L and weigh them. Re-connect K and L, close valves (1) and (2), introduce into C 90 cc. of the solution of Cr<sub>2</sub>O<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> (Reagent 24-a). Insert cork (a) and open valve (3), and as soon as air bubbles appear at K, open valve (1) and slowly admit the solution into D; close valve (1) and apply gentle heat to D, shaking the flask to mix contents. Continue the heat to incipient ebullition. Remove the lamp and gradually open valve (1), till wide-open; when the aspirator O is half empty, open valve (3), so that the air bubbles will come over more rapidly. At first the bubbles should not come over faster than three per second, and at no time fast enough to throw the solution in K into the exit tube. When the aspirator O is nearly empty, close valve (3), and in about five minutes open valve (2); allow the apparatus to stand fifteen minutes, disconnect K and L and weigh them. The increase in weight is CO<sub>2</sub>, of which 27.27 per cent. is carbon.

*Note.*—Use 30 cc. of chromic acid solution for each gram of steel with 1 per cent. of carbon or less. For pig iron, or steels of higher carbon content, use twice the amount per gram.

*Determination of Graphite.*—Take about 2 grams of iron, or 10 grams of steel, add an excess of HCl (sp. gr. 1.12), heat moderately until no more gas is evolved, filter through purified asbestos, wash with hot water, then with a solution of KOH, next with dilute HCl and lastly with hot water. Dry thoroughly and perform the combustion as above.

See, also, method for graphite under Rapid Analysis of Pig Iron.

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### *Colorimetric Determination of Combined Carbon.*

While the colorimetric determination of combined carbon affords a rapid and simple method, it requires considerable practice on the part of the chemist, as well as close attention to details. Results are subject to variation on account of the "personal equation" of the operator.

(*Mr. Textor's Method*).—Steels carrying less than 0.17 carbon are treated by comparison with various standard steels, ranging from 0.05 to 0.17 in carbon. For steels carrying more than 0.17 carbon, the dilution method is used.

(1). *For Steels with less than 0.17 Carbon.*—Treat 0.200 grams of the borings or lump in a flat-bottomed tube, provided with a 3 cc. mark, with exactly 3 cc. of HNO<sub>3</sub>. (The tube used is about  $\frac{5}{8}$ -inch in diameter, and 6 inches long.) When the metal is dissolved and the solution cooled, the color or amount of carbon is "guessed," and the standard steels which are supposed to approximate the carbon content of the unknown steel are weighed, 0.200 grams each. Thus, if the unknown appears to show about 0.12 carbon, the standard a few points below and the standard a few points above, as well as a standard 0.12, are weighed. The three standards are placed in tubes similar to that of the unknown, and dissolved in exactly 3 cc. of HNO<sub>3</sub> (sp. gr. 1.20). Place the four tubes in a water bath, heated to about 95° C. (Various forms of special water baths are used.) The tubes should be labelled or numbered. The solutions are digested from 12 to 15 minutes, or longer if necessary, to obtain a clear solution. Remove the tubes from the bath,

shake to wash down any iron salt adhering to the sides, and stand in cold water. Add sufficient  $\text{HNO}_3$  (sp. gr. 1.20) to each tube, to bring its contents up to 3 cc. and mix well. Now compare in a camera. Suppose standards containing respectively 0.08, 0.11 and 0.14 carbon were used. If the unknown stands in color between the 0.08 and 0.11 and, if it is nearer like the 0.08, call it 0.09 carbon; if it is nearer like the 0.11 standard call it 0.10, and so on.

(2). *For Steels with from 0.16 to 0.30 Carbon.*—Use a standard between 0.20 and 0.30 carbon. Weigh 0.200 grams of each, the unknown and the standard; dissolve in a similar manner to the above, with 3.5 cc. for the standard and 3 cc. for the unknown, of  $\text{HNO}_3$  (sp. gr. 1.20), heat at  $95^\circ \text{ C}.$ , cool when clear.

Pour the standard into a dilution tube, which should be of the following dimensions: one-half inch outside diameter,  $13/32$  inches inside diameter, graduated to 16 cc. in tenths. Both dilution tubes should be of exactly the same dimensions.

Rinse out the solution tube with four or five drops of  $\text{HNO}_3$  (sp. gr. 1.20), add washings to dilution tube. If the standard steel is a 0.25 carbon, dilute it with  $\text{HNO}_3$  (1.20 sp. gr.) to 5 cc. Place the solution of the unknown in the other dilution tube; compare, in the camera, with the standard, adding  $\text{HNO}_3$  (sp. gr. 1.20) a little at a time, and shaking after each addition until the colors agree. The air bubbles must be permitted to rise and escape before comparison. The number of cc. to which the unknown steel was diluted, divided by two, indicates the per cent. of carbon; each cc. representing 0.05 per cent.

(3). *For Steels with from 0.30 Carbon upward.*—One-tenth of a gram is taken of unknown and standard, and the solution made in tubes four inches long by one-half inch internal diameter, with walls about one millimeter thick, using  $\text{HNO}_3$  (sp. gr. 1.20) according to the amount of carbon, as follows:

C. % in Un-known.	HNO <sub>3</sub> , cc.	Standard C. %.	cc. of HNO <sub>3</sub> to Standard.
0.30 to 0.35 . . .	2.5 . . .	0.40 to 0.60 . . .	3.5
0.35 to 0.45 . . .	3. . . .	0.40 to 0.60 . . .	3.5
0.45 to 0.55 . . .	3.5 . . .	0.40 to 0.60 . . .	3.5
0.55 to 0.65 . . .	3.5 . . .	0.50 to 0.70 . . .	3.5
0.65 to 1.25 . . .	4. . . .	0.80 to 1.00 . . .	4.
1.25 to 2.00 . . .	5. . . .	1.25 to 1.50 . . .	5.
2.00 to 4.00 . . .	5. . . .	2.50 . . .	5.

Dissolve, heat, dilute and compare in dilution tubes as before, except that, as a sample weighing one-tenth gram was taken, dilute the standard *one* cc. for every tenth per cent. of carbon it contains; that is, dilute a 0.50 carbon to 5 cc.; then, every cc. of the unknown after comparison will represent 0.10 per cent. of carbon.

Turbidity is sometimes caused by impurities, such as graphite or tungstic acid; in such cases heating longer than fifteen minutes is not necessary.

*Precautions Necessary.*—(1). The standard and the unknown must receive the same treatment throughout the operation, so far as heating, exposure to light and time of standing before and after placing in the bath is concerned. It will not do to heat the unknown for the specified time

and then, if by accident the standard is lost, weigh, dissolve and heat a new standard by itself. The two steels must be both started anew.

(2). The solutions of steel should be kept from direct sunlight, and in the darker portion of the room, while cooling.

(3). The determination should not be delayed for any length of time after once adding the acid, but should be carried to a conclusion without unusual delay.

(4). The steel should not be in a hardened or tempered state, nor should it have been quenched with water or cooled in a blast, during its cooling from a high heat. Open-hearth and Bessemer steels should be in an annealed state, when the carbon is over 0.25 per cent., to insure accurate work. Annealing sometimes causes a separation of graphite in crucible steel, more especially when the mass is large; therefore, small pieces only should be annealed in lime. The crucible steel bars, as they are put upon the market, are usually in a proper state for a colorimetric test.

(5). Steel frequently shows considerable lack of homogeneity in carbon content, and widely differing results may be obtained by taking drillings from different parts of an ingot, billet or even small section. Usually the portion corresponding to the core of the ingot shows higher carbon in the same piece than the surface portion.

*Determination of Tungsten in Steel.*

(This method will also suffice for the exact determination of silicon in tungsten steel.)

Place 2 grams of the steel in a pint beaker, add 40 cc. of  $\text{HNO}_3$  (sp. gr. 1.20), and heat on the hot plate. When the solution is reduced in volume to from 20 to 30 cc. add 10 cc. of strong  $\text{HCl}$  (sp. gr. 1.20); this will immediately throw down  $\text{WO}_3$ . Evaporate to dryness, and heat till odor of  $\text{HCl}$  entirely disappears, cool, add 5 cc. of  $\text{HNO}_3$  (sp. gr. 1.42), then add 15 cc. of strong  $\text{HCl}$ , and heat till dissolved. Add 35 cc. of  $\text{HNO}_3$  (sp. gr. 1.42), heat for 15 minutes, add 75 to 100 cc. of distilled water, stir and filter on an 11 cm. heavy ashless filter (S. & S. No. 589, black or white ribbon). If the first portion of the filtrate is cloudy, re-filter it. Wash with a solution of 1%  $\text{HNO}_3$  in water, seven or eight times. If any precipitate adheres to the beaker, and cannot be rubbed off, dissolve in a few drops of  $\text{NH}_4\text{OH}$ , place in a weighed platinum crucible, evaporate to dryness, then add the washed precipitate. Ignite filter and contents with a gentle heat, finishing with full Bunsen flame; *never with blast*. Cool and weigh; add 10 drops of  $\text{HF}$ , evaporate to dryness, cool, and weigh again; the loss being silica. Of the weight of  $\text{WO}_3$  found, 79.31% is metallic tungsten.

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*Determination of Molybdenum in Steel.*—\*Not more than 1.308 grams of steel are treated with a large excess of strong  $\text{HNO}_3$  and a little potassium chlorate (if chromium is present, as is usually the case); the  $\text{HNO}_3$  is evaporated off, boiled with strong  $\text{HCl}$ , and evaporated to dryness to sep-

\*George Auchy., Journal American Chemical Society, XXIV, 3, p. 273.

arate silica; again taken up with strong HCl and evaporated to first appearance of scum. Then add 5 cc. of strong HCl diluted to 20 cc. with water, and heat to complete solution. the volume of the liquid is made up to 50 cc. and poured, little by little, with shaking, into a solution containing 20 grams of NaOH dissolved in 100 cc. of water, in a 12-ounce Erlenmeyer flask provided with a 300 cc. mark. The liquid is diluted to 300 cc. and mixed by shaking around in the flask, allowed to settle, and filtered into a 250 cc. measuring flask, until it reaches that volume. It is then transferred to a beaker, acidified with H<sub>2</sub>SO<sub>4</sub>, boiled down to less than 100 cc., and finished as in phosphorus determinations, by reducing with zinc and titrating with permanganate.

In this determination, a blank test, upon a steel free from molybdenum, is highly important. It must be made in exactly the same way as given above, using the same amount of HCl and the same amount of chromium; since both affect the accuracy of the determination,—the former very greatly and the latter slightly.

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#### *Determination of Nickel in Nickel-Steel and Ferro-Nickel.*

This is an excellent method.\* The following precautions should be observed: Keep the volume of the iron solution down before using the ether in separatory funnel. Also remember that it is not necessary to separate *all* of the iron; the design being to remove only the greater part, the nickel being then completely separated by two quickly-made ammonia precipitations of the iron.

Dissolve 2 grams of the steel in HCl (sp. gr. 1.10), add 1 cc. of strong HNO<sub>3</sub> to oxidize iron, and evaporate to hard dryness. Take up the residue in 20 cc. of HCl (sp. gr. 1.10),

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\*G. W. Sargent, Journal Analytical Chemistry, Vol. XXI, p. 854.

evaporate to 10 cc. volume, and transfer the solution to a 250 cc. separatory funnel. Use warm HCl (sp. gr. 1.10) for washing the contents of the beaker into the funnel, taking care to keep the volume as small as possible. Cool the funnel and its contents under the spigot, then introduce 40 cc. of ether free from alcohol, which has just been thoroughly shaken with 5 cc. of strong HCl, and shake vigorously for ten minutes, keeping the temperature from rising by frequently holding the funnel under the running water. Allow the funnel to stand a few minutes, draw off the lower aqueous layer containing the nickel, copper, manganese and other chlorides not held by the ether, wash down the sides of the separatory funnel with HCl (sp. gr. 1.10), shake with the ether, and run the washings into the beaker with the chlorides of nickel, copper, etc. Two washings with 5 to 10 cc. of HCl are sufficient to completely remove the nickel and other chlorides from the funnel. The ethereal solution containing the ferric chloride is run into a residue bottle, and the ether is afterward recovered by distillation. Boil the liquid containing the nickel to completely expel the ether, and add to the boiling solution, diluted to at least 200 cc., an excess of ammonia and 10 to 20 drops of bromine water, to precipitate any iron or manganese. Filter, wash, re-dissolve the precipitate in HCl, re-precipitate with ammonia and bromine water, and filter. Combine the filtrates, boil, remove any precipitate, acidulate with HCl, boil until the excess of bromine is expelled, and precipitate the copper as sulphide. The filtrate from the copper sulphide, which contains nickel only, is evaporated to a volume of 100 cc., cooled, and 1 cc. excess of ammonia added. Now introduce into the nickel solution (which is best contained in an Erlenmeyer flask) 5 cc. of silver nitrate solution (0.500 grams AgNO<sub>3</sub> to 1 litre of

water) and the same amount of a 2% solution of potassium iodide. Run into the opalescent solution (which should have a temperature slightly lower than that of the hand) standard potassium cyanide (1 cc. equal to about 0.001 gram of nickel) until the liquid becomes clear and bright. This titration is best made with a black background, when the end reaction becomes very sharp and decided after a little practice, half a drop only being sufficient to discharge the opalescence.

The KCN solution is standardized by introducing into an Erlenmeyer flask 10 cc. of a solution containing a known amount of re-crystallized nickel nitrate [ $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ], 10 cc. of HCl (sp. gr. 1.10), 1 cc. excess of  $\text{NH}_4\text{OH}$ , and 5 cc. each of the silver nitrate and KI solutions, diluting the whole to 100 cc., and running in the standard KCN until the solution clears. It is necessary that a blank titration be made upon the silver nitrate and potassium iodide used as an indicator, under the same conditions as used in the ordinary titration, that a correction factor be determined for use in each titration.

*Examination of Ferro-Nickel.*—Dissolve 20 grams of the sample in aqua regia, evaporate to hard dryness, take up with HCl (sp. gr. 1.10), transfer to a litre flask, and dilute to the mark with water. Take 50 cc. of this solution, add 5 cc. of strong HCl, and concentrate to one-sixth of its volume. Transfer to the separatory funnel, and proceed as with steel.

In the above analyses, if copper is known to be absent, the use of hydrogen sulphide can be omitted.

*Analysis of Ferro-Tungsten.*—\*To avoid damage to platinum crucible and obstruction in the analysis by use of a nickel crucible, the prepared sample is fused in a copper crucible, as follows: Thoroughly mix 0.500 grams of the material with exactly 3 grams of sodium peroxide in the crucible, and fuse for about one minute at a dull red heat, holding the crucible in a pair of tongs and agitating slightly to prevent agglomeration; cool, dissolve in a covered dish with hot water, wash the crucible into the dish, add a few cc. of alcohol to the solution in the dish, and heat to render manganese insoluble; filter with pump and wash with hot water. If decomposition is complete, all of the tungsten will be in the filtrate, and all of the iron, manganese and copper will remain on the filter. A part of the silica will be in the filtrate, and a part with the residue. Transfer the filtrate to a 6-inch evaporating-dish, acidify with HCl and evaporate to dryness on the hot-plate to render silica and tungstic acid insoluble; take up with 15 cc. of HCl and evaporate to dryness again; take up with 15 cc. of HCl, add 100 cc. of water, boil for a few minutes, filter with suction, and wash with a 10% solution of nitric acid. Test the filtrate for tungsten by another evaporation to dryness.

During evaporation of the filtrate, dissolve the residue on the filter in hot dilute  $\text{HNO}_3$ , and evaporate to dryness; take up in HCl and water, filter through the filter upon which is the tungstic acid, washing with 10% nitric acid. Ignite, cool and weigh as  $\text{WO}_3 + \text{SiO}_2$ , add  $\frac{1}{2}$  cc. of  $\text{H}_2\text{SO}_4$  and about 5 cc. of HF, evaporate slowly to dryness, then ignite strongly, cool and weigh; calculate the loss to silicon, and the remainder to metallic tungsten. Clean the crucible by fusing

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\*A. G. McKenna, Eng. & Mg. Journal, Vol. LXVI, page 607.

therein 2 grams of  $\text{Na}_2\text{CO}_3$  and solution in water. If nothing but tungstic acid was present, a clear and colorless solution will occur. The filtrate containing iron and manganese may be examined for these metals by the usual methods.

The author says that the above method answers very well when the ferro-tungsten contains no appreciable amounts of other metals, but that it is not unlikely to contain chromium and aluminum; in which case the chromium and most of the aluminum go into the soluble part of the fusion. After the tungsten has been separated by evaporation to dryness, the chromium and aluminum may be precipitated by  $\text{NH}_4\text{OH}$ ; after ignition, cooling and weighing, the combined oxides are dissolved in a small flask with  $\text{HNO}_3$  and  $\text{KClO}_3$ , the alumina is precipitated with  $\text{NH}_4\text{OH}$ , filtered and determined, and the chromium in the filtrate precipitated and weighed as chromic oxide.

A weighed amount of the sodium peroxide is used in the fusion, since that salt always carries silica and iron, and these must be determined and a proper correction made therefor.

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*Determination of Copper in Iron and Steel.*—Dissolve from 5 to 10 grams of the sample in a 10% solution of  $\text{H}_2\text{SO}_4$ , dilute to 400 or 500 cc. with water, boil and add (without filtration) a solution of sodium thio-sulphate, according to the method given for the precipitation of copper in the Analysis of Brass (Part I, Gravimetric Separations). Filter, wash with hot water, dry, ignite filter separately, combine ash and residue, and treat with aqua regia; finally add 1 cc. of  $\text{H}_2\text{SO}_4$  and evaporate till white fumes arise, cool, take up in water, and determine copper by electrolysis or otherwise.

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*Determination of Arsenic.—Lundin's Method.* Dissolve 10 grams of drillings in a large beaker in  $\text{HNO}_3$  (sp. gr. 1.20), transfer the solution to a platinum or por-

celain dish, add 50 cc. of  $H_2SO_4$ , and evaporate till copious fumes of sulphuric acid are given off. Cool, add 50 cc. of water, and evaporate until the excess of  $H_2SO_4$  is expelled and the ferric sulphate is so dry that it may be easily transferred to a half-litre flask. To the mass in the flask add 15 grams of finely powdered ferrous sulphate, pour in 150 cc. of strong HCl, and close the flask with a stopper carrying an exit-tube bent twice at right-angles and connected by a rubber tube with a 50 cc. pipette, the point of which dips about  $\frac{1}{2}$  inch into 300 cc. of water in a beaker. Heat the material in the flask gradually until it boils, and continue the distillation until the wide part of the pipette becomes heated. The arsenic acid is reduced by ferrous sulphate, and, in the strong HCl solution, is distilled into the beaker as arsenious chloride. When distillation is complete, or in about one-half hour, heat the contents of the beaker to about  $70^\circ C.$ , and pass through it a rapid current of  $H_2S$  to complete saturation. Remove the excess of  $H_2S$  by a current of  $CO_2$ , and filter off the arsenious sulphide in a Gooch crucible or on a weighed filter; wash with water, then with alcohol, then with pure  $CS_2$ , dry at  $100^\circ C.$ , and weigh.

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### Phosphorus in Iron Ores and Products.

Although the method of determining phosphorus by the weight of the magnesium pyro-phosphate has been superseded in commercial laboratories by the more rapid "direct" and volumetric methods, the method is considered worthy of insertion, since in remote cases it may serve as a check on later and more rapid methods, although its general use is not to be recommended. The method as herein given was carefully worked out by Professor Cheever.

(1). *For Iron Ores.*—Weigh 5 grams of the fine dry ore and digest at  $100^\circ C.$  with strong HCl till all, or nearly all,

is dissolved; boil for fifteen minutes, filter and wash slightly. Place the filter and its residue in a platinum crucible and incinerate thoroughly; cool, add dry  $\text{Na}_2\text{CO}_3$  and fuse; dissolve in dilute HCl and add this solution to the former filtrate. Evaporate to dryness, and heat at  $110^\circ \text{ C}$ . till it no longer emits an odor of HCl; cool slightly, add strong HCl and boil till the iron is dissolved. Evaporate as low as possible without formation of iron oxide, add 30 cc. of  $\text{HNO}_3$  (sp. gr. 1.42) and evaporate to a syrupy consistence; add more strong  $\text{HNO}_3$  and repeat till all the HCl is driven off; add an equal volume of water, cool and filter. This filtrate should be concentrated to not over 100 cc. in bulk. It is further treated as directed under Irons and Steels, see (X) below.

(2). *For Irons and Steels.*—Take for analysis, of Bessemer or other low-carbon steels, from 3 to 5 grains; of crucible steel, 10 grams; of pig iron, from 1 to 5 grams, according to the percentage of phosphorus supposed to be present; of iron high in phosphorus (1 per cent.), take 1 gram. Place in a No. 4 evaporating dish, cover with a funnel which will fit inside of the dish, and add gradually  $\text{HNO}_3$  (sp. gr. 1.20), using 12 cc. of acid for each gram taken, unless the sample should happen to be very small.

When the full amount of acid has been added, and violent action has ceased, add 10 cc. of  $\text{HNO}_3$  (sp. gr. 1.40) and boil down to one-half. Add 10 cc. more of strong  $\text{HNO}_3$ , continue boiling and add, in small portions, at intervals, about 2 grams of pulverized  $\text{KClO}_3$ . If the solution shows signs of going dry add more strong acid. Manganese will be precipitated with some iron. If the manganese does not come down readily, add more  $\text{KClO}_3$ . The process is not

complete till a dark, mirror-like deposit appears on the dish at the edge of the solution. Boil five minutes after the last addition of  $\text{KClO}_3$ , and add, cautiously, sufficient HCl to dissolve the iron and manganese. Expel all the chlorine by boiling, adding strong  $\text{HNO}_3$ , from time to time, to avoid dryness. Add an equal bulk of water to the solution, boil a few minutes and filter into a flask, when the solution should not exceed about 100 cc. in bulk.

(X). Gradually add strong  $\text{NH}_4\text{OH}$  till the solution becomes pasty; add strong  $\text{HNO}_3$ , cautiously, till the mass is dissolved and the solution has a light straw color on cooling to 60° C. If the solution has a decided red color, iron will be thrown down with the phospho-molybdate precipitate. If the solution is red, add more strong  $\text{HNO}_3$ . The solution should not now exceed 200 cc.

At 60° C. add 60 cc. of molybdate solution (Reagent 6-b), cork the flask and shake violently for five minutes; let stand at 60° C. till the precipitate settles.

Filter through a four-inch filter and wash the precipitate with an acid solution of  $\text{NH}_4\text{NO}_3$  (Reagent 8) or with 2 per cent.  $\text{HNO}_3$ , till the wash water gives no trace of iron.

[\*In the case of pig iron, Von Reiss found that the magnesium pyro-phosphate always contained iron. To avoid this, after washing the phospho-molybdate precipitate with  $\text{HNO}_3$ , as above, drop on the filter, from a pipette, 15 cc. of a solution consisting of 10 grams of citric acid dissolved in 100 cc. of  $\text{NH}_4\text{OH}$ , then wash with 2½%  $\text{NH}_4\text{OH}$ , and proceed as follows:]

Dissolve the precipitate on the filter with a 3 per cent. solution of  $\text{NH}_4\text{OH}$ ; the filter should remain perfectly white, or only slightly tinged with red on its upper edge. If much colored with iron, wash into the filtrate with dilute  $\text{HNO}_3$ .

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\*Classen, 298.

sufficient to render the filtrate acid, add 5 cc. of molybdate solution, heat to 80° C., let stand fifteen minutes, filter and wash as before. Dissolve in 3 per cent.  $\text{NH}_4\text{OH}$ .

To the ammoniacal solution add 5 cc. of strong HCl, or enough to render the solution acid; dissolve this precipitate with  $\text{NH}_4\text{OH}$ , adding it gradually, so that the last drop will just disperse the yellow color, leaving the solution cloudy and with a peculiar, sweet smell. Boil ten minutes; set aside till the silica becomes flocculent, and filter through a small, close filter.

By repeated tests, phosphorus was not found in the separated silica when iron was not present, but the reverse is true.

To the filtrate add 5 cc. of  $\text{NH}_4\text{OH}$ , make thoroughly cold and add gradually 15 cc. of magnesia mixture (Reagent 3), keeping the solution in constant motion; cork the flask and shake violently for two or three minutes; set aside for three hours, filter and wash with 25 per cent.  $\text{NH}_4\text{OH}$ .

Place the moist precipitate, with the filter, in a platinum crucible; cover, and apply a strong heat till the filter is thoroughly charred. Remove the cover, turn the crucible on its side, and ignite till the residue is white. The determination may be made in six hours. Result equals  $\text{Mg}_2\text{P}_2\text{O}_7$ . Of this 27.83 per cent. is phosphorus.

### Technical Analysis of Blast Furnace Slag.\*

Of the various constituents of a slag, the blast-furnace manager usually requires only the determination of the Silica, Alumina, Lime, Magnesia and Sulphur. The following method includes only the determination of those substances, and is given in detail, to show the laboratory manipulation used in the analysis of a sample of slag.

*Operation.*—For silica and alumina place 0.500 grams in a pint beaker marked  $\text{SiO}_2$ . For lime and magnesia place 1.325 grams in a pint beaker marked  $\text{CaO}$ .

Add 20 to 25 cc. of hot water to each beaker; give the liquid a rotary motion to stir up the slag; bring rapidly to a boil over a bare flame; add to the  $\text{SiO}_2$  beaker 10 cc. of dilute HCl (sp. gr. 1.12) and keep the liquid in motion till the fine slag particles are dissolved. If the liquid is not kept in motion the acid liberates gelatinous silica, which surrounds small particles of slag, rendering decomposition difficult. If properly added, the acid produces a clear or slightly turbid solution, the turbidity being due to finely divided, insoluble, suspended matter, free sulphur, or carbon.

The beaker marked  $\text{CaO}$  is treated in the same manner, except that 15 or 20 cc. of dilute HCl are added instead of 10. The two solutions are boiled till the slag is dissolved.

The  $\text{SiO}_2$  solution is evaporated as low as safety will permit over the bare flame, two or three drops of  $\text{HNO}_3$  are added, and the beaker placed on the iron plate, where it is left until all visible signs of moisture disappear; it is then transferred to a previously heated asbestos board, and a strong heat is continued till the residue is dry or fumes of HCl can no longer be detected.

During this time the  $\text{CaO}$  beaker is removed from the

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\*Rapid method, by Mr. Textor.

heat, and to the hot solution are added 15 cc. of strong HCl containing four or five drops of HNO<sub>3</sub>; the HNO<sub>3</sub> oxidizes the ferrous iron. Pour in cold water up to 300 or 350 cc., stir and add slowly, 5 cc. at a time, 25 cc. of strong NH<sub>4</sub>OH, which precipitates the silica and alumina. The NH<sub>4</sub>OH must be added in this manner so that some NH<sub>4</sub>Cl may be formed to hold the magnesia in solution and prevent its precipitation with silica and alumina.

Pour the liquid with the precipitate into a flask marked on the neck at 530 cc.; fill to the mark and mix. Filter through a large, dry paper in a five-inch, ribbed funnel.

The first 250 cc. of the filtrate, representing 0.625 grams of the slag, transfer to a pint beaker marked MgO.

The next 200 cc. of the filtrate, representing 0.500 grams of the slag, is poured into a beaker marked CaO.

Bring the contents of both beakers to a boil, add to the magnesia portion 25 cc. of a saturated solution of (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, and to the lime portion 20 cc. of the same reagent; stir each for a few seconds, then place the magnesia beaker in water to cool.

Filter off the calcium oxalate in the CaO portion at once, wash well with hot water, spread out the filter on the side of the beaker, wash the precipitate off the filter, dissolve it in hot water containing 15 cc. of strong H<sub>2</sub>SO<sub>4</sub>, and titrate with standard KMnO<sub>4</sub>, (Reagent 28), as under Analysis of Lime-stone.

When the beaker containing the magnesia solution is cool, pour its contents into a flask with a 300 cc. mark on its neck, fill to the mark and thoroughly mix. Filter through a heavy, dry paper in a five-inch, ribbed funnel; 240 cc. of the filtrate, representing 0.500 grams of slag, are poured into a pint beaker, into which has been previously put 10 cc. of sodium

phosphate solution (30 grams to 250 cc. of water) and 10 or 15 cc. of strong  $\text{NH}_4\text{OH}$ ; or, use an Erlenmeyer flask instead of a beaker. Agitate for ten minutes to precipitate the magnesia, with a shaking machine if a flask was used, or by blowing air through the liquid by means of a blast arrangement if the beaker was used for the precipitation.

By this time the silica and alumina residue has become thoroughly dry; the beaker is removed from the light, and in order to avoid breaking by standing on the cold table, and yet cool rapidly, the beaker is suspended in a wire beaker holder. When cool, about 15 cc. of strong HCl is poured on the residue, and the beaker replaced on the hot asbestos board.

The magnesia precipitate is now filtered and washed as usual with weak ammonia water. The wet filter containing the phosphate is placed in a crucible and put over a Bunsen flame, only the point of the flame touching the crucible; this dries and chars the filter rapidly. When the paper is partly charred, cool the crucible, shake out the precipitate into the bottom, put the paper back and ignite strongly. Cool in a desiccator and weigh.

The silica beaker with the HCl has now stood on the asbestos board about five minutes; add 25 cc. of hot water and boil the solution for another minute. Filter through an ashless, 9 centimeter paper, supplied with a platinum cone. After the liquid has run through, rinse the silica from the beaker into the funnel. Do not use a rubber to remove the particles adhering to the beaker, but simply rinse out with hot water, filling the filter four or five times with the rinsings.

The alumina is now all contained in the filtrate, which is placed over the open flame to boil.

The silica is cleaned out of the beaker with a rubber and,

as the finely divided precipitate now clogs the pores of the paper, suction may be applied to hasten filtration. More washing of the silica is unnecessary, and the wet paper is put into a crucible and ignited.

When the alumina solution begins to boil, add strong  $\text{NH}_4\text{OH}$  in excess, a few cc. at a time, stirring well after each addition, to form  $\text{NH}_4\text{Cl}$  to prevent the precipitation of magnesia. Filter immediately, without suction at first, through an ashless paper, 11 centimeters in diameter, supplied with a platinum cone. If the filter is thick and the funnel a good one, the filtration proceeds rapidly at the outset. When the last portion of the liquid has almost all passed the paper, apply suction, which is increased and continued till the precipitate becomes shrivelled and furrowed over its whole surface, taking perhaps a minute.

The washing will now proceed rapidly, as the bulky and slimy precipitate has been contracted to a small volume by the strong and continued suction. Filling the filter four or five times with hot water suffices for the washing. Ignite and weigh as alumina.

As the slag usually contains but low percentages of iron, that element is weighed with the alumina, and the whole reported as such; iron may, however, be rapidly determined by dissolving one gram of the slag in the manner indicated, using 50 to 75 cc. of water, boiling to expel sulphuretted hydrogen, adding one or two drops of stannous chloride, cooling, adding mercuric chloride and manganous sulphate solutions, and titrating with standard  $\text{KMnO}_4$ .

For sulphur, weigh 0.500 grams into an ordinary tumbler, as that is less liable to be broken than a beaker by the stirring rod. Add about 150 cc. of hot water and some starch solution. Now add about 15 cc. of standard iodine solution

(Reagent 23); then add 15 to 20 cc. of strong HCl and stir. The slag soon dissolves with a little stirring; the sulphuretted hydrogen liberated is oxidized by the iodine solution, which is added to the end reaction. One cc. of iodine equals 0.1 per cent. of sulphur when 0.500 grams of the substance are taken.

The small amount of manganese present in the slag is not determined; it appears in part in the magnesium pyro-phosphate residue.

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In *Refinery Slags* it is frequently desirable to determine the amount of metallic iron; this can be conveniently accomplished as follows:—

Digest 5 grams of the slag, which has been previously pulverized and dried at 100° C., with a 1% solution of copper sulphate in water; the operation being carried on in a platinum dish. If metallic iron is present, metallic copper will be deposited in amount equivalent to the metallic iron, according to the equation:  $\text{CuSO}_4 + \text{Fe} = \text{FeSO}_4 + \text{Cu}$ . The residue may be washed, the copper dissolved and determined volumetrically.

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#### Analysis of Coal and Coke.

For practical purposes, the determination of moisture, volatile combustible matter, fixed carbon, ash, and sulphur in sulphides and calcium sulphate, is generally sufficient; to these determinations may be added that of the heating power, which is approximately made by (1), weighing the lead reduced from lead oxide or carbonate by a known weight of the coal or coke, or, with accuracy but less rapidly,

by (2) determining the total carbon and hydrogen by combustion of a sample of the material.

*Moisture.*—Clean, dry and weigh a platinum crucible, place in it a finely pulverized sample of the coal, one gram in weight, and dry in an air-bath at 115° C. for one hour; cool in a desiccator and weigh. The loss in weight equals the moisture.

*Volatile Combustible Matter.*—Take a fresh sample of the coal, place 1 gram in a platinum crucible, adjust the cover and heat in the flame of a Bunsen burner for exactly three and one-half minutes; then, without cooling, heat with the blast for the same length of time, cool and weigh. The loss of weight, less the moisture, equals the volatile combustible matter with some sulphur. This ignition is generally reported to drive off one-half of the sulphur present in combination with iron pyrites.

*Fixed Carbon.*—Carefully ignite the residue from the last operation until the carbon is burned off, cool, weigh, and repeat the operation till constant weight is obtained. The loss equals the fixed carbon and some sulphur. This ignition is generally reported to drive off the remaining half of the sulphur present in combination with iron as pyrites.

*Ash.*—The residue from the last ignition is reported as ash. It may be dissolved and analyzed by the usual processes for phosphorus and other metals.

\**Total Sulphur.*—Thoroughly mix 4 grams of MgO with 2 grams of Na<sub>2</sub>CO<sub>3</sub> and determine the sulphur in the mixture. Take 2 grams of this mixture; mix the greater part of it with 1 gram of the coal or coke, very finely pulverized, in a platinum crucible, and place the re-

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\*Eschka's method.

mainder on top of the charge. The crucible should not be over two-thirds full. Place the crucible in an inclined position and heat very gradually, with an alcohol lamp, or with a flame containing no sulphur, until finally the bottom of the crucible is a dull red. The mass must not fuse.

Stir the contents of the crucible with a platinum wire to hasten the combustion. When the carbon is all burned off, remove the lamp and cool the crucible; when cold add 1 gram of pulverized  $\text{NH}_4\text{NO}_3$ , mix thoroughly and heat for ten minutes at a red heat. Cool, dissolve in water, transfer to a beaker, dilute and filter. Acidulate with  $\text{HCl}$  and add to the boiling filtrate a boiling solution of  $\text{BaCl}_2$ , allow to stand one hour, filter and determine the sulphur from the weight of the barium sulphate.

*Determination of Sulphur. (Rapid Method\*).*—Mix 0.500 grams of the finely powdered material with  $\frac{1}{3}$  grams of sodium peroxide, and place in a steel crucible of from 60 to 80 cc. capacity and which is provided with a cover through which is a small perforation. The sodium peroxide should be dried, finely powdered, and thoroughly mixed with the coal or coke. Adjust the cover, and place crucible and contents in a small graniteware dish, to which water is added to about the height of one inch. Ignite the contents of the crucible by inserting a red-hot wire through the perforation in the cover. After a few minutes combustion, lay the crucible on its side, so that the water in the dish may dissolve the contents. Wash crucible and cover carefully, and transfer contents of dish to a beaker; make slightly acid with  $\text{HCl}$ , boil, filter and wash. Precipitate the sulphuric acid in this filtrate in the usual way.

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\*C. Sundstrom, Journal Am. Chem. Soc., XXV, 184.

*Volumetric Sulphur.*\*—Treat the coal or coke as in the manner preceding, until the solution is made acid; at this point, make distinctly acid with HCl and boil; add ammonia till slightly alkaline, and boil again; then add 15 cc. of barium chromate solution (Reagent 36) and boil for one minute. Add water to bring the volume of the solution to 200 cc., then add ammonia to slight excess, and continue the boiling. Allow the precipitate to settle, filter and wash with hot water; washing twice, using 20 to 30 cc. of hot water each time. To the filtrate add 1 gram of KI, cool to 30° C. and add 5 cc. of HCl. Titrate with standard thio-sulphate solution, using starch indicator; or, excess of thio-sulphate may be added and the excess titrated with standard iodine. If a 0.500 gram sample is taken, the number of cc. of n/10 thio-sulphate used, if multiplied by 0.2137, equals the per cent of sulphur.

*Sulphur Present as Calcium Sulphate.*—Take 4 grams of the coal, add 6 grams of Na<sub>2</sub>CO<sub>3</sub> (which must be free from sulphur), place in a No. 2 beaker, add 50 cc. of water and boil for two hours, replacing the evaporated water. Filter, acidulate with HCl and precipitate the sulphuric acid in the usual manner.

†*Heating Power.* (1) *By reduced lead.*—The lead assay may be made as follows:

Intimately mix, by grinding in a mortar, 0.200 grams of the finely powdered coal with 10 grams of dry lead carbonate. Place this mixture in a short tube of combustion glass, about 5½ inches long, by 6/10 inches internal diameter, in which has already been placed 0.300 grams of borax glass. Cover to a depth of 2½ inches with grains of lead carbonate which

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\*Modification by J. D. Pennock and D. A. Morton.

†R. C. Hills, Proc. Colo. Sci. Soc.

will not pass a 60-mesh sieve, and adjust a loose cap of thin sheet-iron on the open end of the tube. This tube is placed in an upright position in a 5-gram clay crucible, being supported by an inverted scorifier which fits into the mouth of the crucible and has a hole drilled through it to allow the passage of the tube. Place in a muffle which has scarcely attained a red heat, and gradually raise the heat for twenty minutes, then heat strongly for about ten minutes, cool, break and weigh the resulting lead button.

*Calculation.*—When calculating the calorific power of a fuel from the results obtained by this method, some account must be taken of the kind of fuel operated upon. In the case of charcoal, coke, and the better qualities of anthracite, it may be sufficient for practical purposes to assume, as is ordinarily done, that the reduced metal represents a certain number of carbon heat units, or, in other words, to compare its value with that of pure carbon; but in an assay of bituminous, semi-bituminous and sand coals, or lignite, it will be advisable to make a correction for hydrogen; otherwise the value, as compared with that calculated from an ultimate analysis, will be too low by from 100 to 400 heat units, according to the character of the coal. If the relative proportions of carbon and hydrogen in coal were always the same, the amount of reduced lead would indicate very closely the comparative heating power; but the proportions of available hydrogen in different kinds of coal may vary as much as 3 per cent., or even more in extreme cases, so that the reduced lead simply indicates the capacity of the fuel for oxygen. Mück\* states that the average amount of disposable hydrogen in the different kinds of coal is as follows: Lignite,

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\*Steinkohlen Chemie.

3 per cent.; gas coal, 4.5 per cent.; coking coal, 4.5 per cent.: semi-caking and sand coal, 3.5 per cent: and anthracite, 1.5 per cent. Though these figures may not be generally applicable to all coals, they may be considered as representing approximately the available hydrogen in the different kinds of coal, and used as follows: One part of lead reduced by carbon corresponds to  $8080 \div 34.5 = 234$  carbon calories. One part of lead reduced by hydrogen corresponds to  $34462 \div 107 = 322$  hydrogen calories; one part of carbon reducing 34.5 parts of lead, and one part of hydrogen reducing 107 parts of lead. Suppose a certain coking coal yielded upon assay 31 times its weight of lead; by Mück's figures this should contain 4.5 per cent. of disposable hydrogen; if one part of hydrogen reduces 107 parts of lead, 4.5 per cent. will reduce  $107 \times .045$  or 4.815 parts of lead. Subtracting this from the whole number of parts of lead reduced (31), we have remaining 26.185 parts of lead which was reduced by the carbon. Since 26.185 parts of lead reduced by carbon correspond to  $26.185 \times 234 = 6127.4$  heat units, and 4.815 parts of lead reduced by hydrogen correspond to  $4.815 \times 322 = 1550.5$  heat units, we have altogether 7677.9 heat units as representing the available heating power of the coal.

Should it be desirable to make anything more than a close approximation, the heating power may be closely estimated by the use of the absolute percentages of carbon and hydrogen in the coal, which may be determined as follows:

(2) *By Combustion.*—A combustion tube containing ignited CuO, for about one-half the length of the tube at its exit end, is connected with (1) a calcium chloride tube for absorbing hydrogen as moisture, and (2), a soda-lime tube for absorbing carbon as carbonic acid gas, and (3), an

aspirator. The other end of the combustion tube is connected, by guard tubes containing respectively strong  $H_2SO_4$ , and strong solution of KOH, with an oxygen tank. The tube is placed in the combustion furnace and a blank combustion made, after which the calcium chloride and soda-lime tubes are weighed. A weighed quantity of the coal is placed in a platinum boat and dried at  $115^{\circ} C.$  for one hour; it is then inserted in the combustion tube, the apparatus is connected, and the coal is slowly and completely burned in a stream of oxygen. When the combustion is complete, the heat and oxygen are shut off and air is aspirated till the apparatus is cool. The hydrogen and carbon are estimated as usual from the increased weights of the calcium chloride and soda-lime tubes.

From the percentages of the above elements the heating power may be accurately determined in Fahrenheit or Centigrade heat units.

Thompson's Calorimeter and other forms are extensively used for determining the heating power of various fuels, from observation of the increase in temperature of a known weight of water due to the combustion of a certain weight of the fuel; but they necessitate the use of correction factors for loss of heat, which vary from 10 to 30 per cent. and which are not constant.\* Mahler's bomb calorimeter probably gives the best results of any.

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\*Kalometrische Untersuchungen. Stohmann, Landw. Jahr. 13, p. 513.

### Water Analysis.

While great advances have been made in the chemical examination of waters, there is yet considerable disagreement as to the interpretation of the results obtained, more especially as affecting the sanitary character of the water. Authorities on the subject differ among themselves, and have invested the matter, beside, with the necessity for complicated and expensive apparatus, to such an extent as to practically place the matter outside the reach of the general chemist.

The consideration in this work is confined to the chemical examination of Mineral Waters and waters for Steam Boilers and other technical purposes, with a short consideration of the examination for poisonous metals. For more extended information upon the subject, reference may be had to Sutton's *Volumetric Analysis* and the works of Wanklyn and Frankland. A most able and practical treatise upon the subject is that of Leffman and Beam,—“*Examination of Water for Sanitary and Technical Purposes.*”

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*Combination of Bases and Acids.*—When the bases and acids have been estimated in a sample of water, the usual method of combining them, as they are supposed to exist in the water, is as follows: The chlorine is combined as far as it will go, with (1) sodium, (2) potassium, (3) magnesium, and (4) calcium. The sulphuric acid is united after the chlorine has been saturated, with (1) sodium, (2) potassium, (3) calcium, and (4) magnesium. The carbonic acid is combined, lastly, with calcium and magnesium. Generally this method should not be used, but rather report the bases found as elements and the acids as acid radicals.

*Report of Results.*—The results should be reported as “parts per 100,000” and also as “grains per gallon.” The U. S. gallon contains, at 15.5° C., 58318 grains of distilled water; the British gallon contains 70000 grains. Using the metric system we obtain results in milligrams; then *centi-*

grams per litre will correspond to "parts per 100,000"; or, every ten milligrams per litre correspond to one part per 100,000, and every part per 100,000 multiplied by 0.58318 equals grains per U. S. gallon.

*Collection of Samples.*—The amount to be collected will depend upon the nature of the water and the number of the elements to be determined; as a rule two gallons will be ample.

Care must be exercised to secure an average sample. The bottle in which the sample is to be collected must first be thoroughly cleaned, then rinsed out with the water to be examined. Fill with the water, close with a clean stopper and seal. Before taking a portion for any determination, the bottle should be well shaken in order to distribute any sediment. Keep the bottle constantly corked when not open for the purpose of removing a sample.

#### *Poisonous Metals.*

Lead, Copper, Arsenic, Zinc and Barium are decidedly poisonous; excess of Manganese and Iron (probably more than 0.5 part per 100,000) is objectionable.

*Lead.*—*Detection by Harvey's Method.*—Place 250 cc. of the water in a conical precipitating jar, add 0.100 grams of  $K_2Cr_2O_7$ , and dissolve by agitation. Treat the same volume of pure water in a similar manner and compare the two solutions. If lead is present it will finally be precipitated, and a very small quantity renders the solution turbid. The reaction will occur with no other metal likely to be present.

*Determination of Lead.*—This may be accomplished by evaporating a large quantity of the water and proceeding by the usual analytical processes; or, if copper be absent,

more simply by a colorimetric test, as follows: Dissolve 0.1596 grams of  $\text{Pb}(\text{NO}_3)_2$  in one litre of water. Each cc. of this solution contains 0.0001 grams of lead. Take 100 cc. of the water, place it in a tall glass cylinder or tube. Similarly arrange 100 cc. of distilled water. Add to each 5 cc. of  $\text{H}_2\text{S}$  solution and a few drops of acetic acid, sufficient to acidify. Agitate each solution, add to the portion of distilled water sufficient of the lead solution to cause a similar tint to that of the water in the other cylinder. From the amount of lead solution added, estimate the lead in the water examined.

*Copper.*—In the absence of lead, copper may be detected and estimated by acidifying the water with acetic acid and adding  $\text{H}_2\text{S}$ , similarly to the colorimetric method for lead: using a standard copper solution containing 0.3984 grams of  $\text{CuSO}_4$  per litre; one cc. equals 0.0001 grams of copper. If lead is present, and not in too large quantity, the copper may be estimated by color titration with  $\text{K}_4\text{FeCy}_6$ , with which lead gives a light colored precipitate. If iron is present it may be removed with  $\text{NH}_4\text{OH}$ .

A solution of  $\text{NH}_4\text{NO}_3$  is prepared, 100 grams to 1 litre of water; also a solution of  $\text{K}_4\text{FeCy}_6$ , 1 gram to 25 cc. of water. The solution to be examined is rendered faintly alkaline with  $\text{NH}_4\text{OH}$ , the excess of which is then boiled off. Salts of sodium and potassium are neutralized by acid and the acid then neutralized by  $\text{NH}_4\text{OH}$ .

*Operation.*—Use two colorimetric tubes of about 150 cc. capacity. Place in one tube a measured quantity of the neutral solution to be tested for copper, fill both tubes to the mark with distilled water and add 5 cc. of  $\text{NH}_4\text{NO}_3$  solution to each. Add, from a burette, to the distilled water tube, small portions of the standard copper solution until

the color in both tubes is alike. From the amount of copper added, compute the result.

*Arsenic.*—This may be detected, if present, by Reinsches copper test. One litre of the water is made alkaline with pure  $\text{Na}_2\text{CO}_3$ , and evaporated nearly to dryness. Place in a test-tube a small piece of bright copper foil, add 3 cc. of distilled water acidulated with HCl and boil gently. If the copper remains bright, add the water residue to the contents of the test-tube, acidify with HCl, and boil for five minutes. If arsenic is present the copper will be colored a steel gray.

*Arsenic, Determination.*—Evaporate one or two litres of the water to dryness, ignite the residue with fusing mixture, extract with water and determine according to the method used in the analysis of Paris Green.

*Zinc.*—This metal is best detected by boiling an ammoniacal solution of the water, filtering and adding a few drops of  $\text{K}_4\text{FeC}_6$ , which produces a white precipitate. Its amount may be determined by evaporation of a sufficient quantity of the water, separation of the zinc, and proceeding by the method given under Analysis of Alloys.

*Barium* is only present in waters containing no  $\text{H}_2\text{SO}_4$ . It may be detected and estimated by precipitating as a sulphate, from a portion of the water acidified with HCl, by addition of a solution of  $\text{CaSO}_4$ .

*Manganese.*—Evaporate one litre of the water to small bulk, nearly neutralize with HCl, and add a few drops of  $\text{H}_2\text{O}_2$ . If  $\text{MnO}_2$  is precipitated, as indicated by a brown color, filter it off and determine its amount by one of the methods elsewhere described in this book.

*Iron* will be detected and estimated in the general quantitative analysis given below.

*General Quantitative Analysis.*

*Determination of Total Solids.*—(a) *In Suspension.*—If there is considerable suspended matter visible, filter one litre of the water through a weighed asbestos filter, wash with distilled water, dry at 130° C., cool and weigh.

(b) *In Solution.*—Place 100 cc. of the water, or a larger quantity in case of purer waters, in a weighed platinum dish and evaporate to dryness on the water bath. Place in the air bath at 130° C. for one hour, cool and weigh. Result, less weight of dish, equals Total Solid Residue. Subtract the weight of the suspended solids to obtain the dissolved solids.

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*Determination of Chlorine.*—Take 100 cc. of the water, place in a porcelain dish, add a few drops of  $K_2CrO_4$  (Reagent 30-b), and titrate with  $AgNO_3$  (Reagent 30-a), till a faint, permanent, red color remains. If good results are not obtained, concentrate 500 cc. of the water by evaporation, cool and titrate as before.

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*Determination of Sulphuric Acid.*—Take 200 cc., acidify with HCl, boil and filter. Precipitate with  $BaCl_2$ , as directed in Part I.

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*Analysis of Water Residue.*—Acidulate one litre with HCl, evaporate to dryness, moisten the residue with HCl, dissolve with water and filter.

*Residue (a).*— $SiO_2$ . Dry, ignite, cool, and weigh.

*Filt. (a).*—Concentrate by evaporation, add excess of  $NH_4OH$ , boil and filter.

Pp. (b) —  $\text{Fe}_2(\text{OH})_6$ ;  $\text{Al}_2(\text{OH})_6$ ;  $\text{P}_2\text{O}_5$ . Wash, dry, ignite and weigh. If desired, this precipitate may be fused with  $\text{Na}_2\text{CO}_3$ , dissolved, and the  $\text{P}_2\text{O}_5$  determined.

Filt. (b).—Add excess of  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ , boil, let stand six hours, filter and wash.

Pp. (c). =  $\text{CaC}_2\text{O}_4$ . Dry, ignite to  $\text{CaO}$ , cool and weigh.

Filt. (c).—Concentrate, cool, add solution of  $\text{Na}_2\text{HPO}_4$  and excess of  $\text{NH}_4\text{OH}$ , let stand six hours, filter and wash.

Pp. (d) =  $\text{Mg}_2(\text{NH}_4)_2(\text{PO}_4)_2$ . Dry, ignite to  $\text{Mg}_2\text{P}_2\text{O}_7$ , cool and weigh.

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*Determination of Lithium, Sodium and Potassium.*—If lithium is suspected, it may be detected by use of the spectroscope, as follows: Evaporate from one to three litres of the water to about 150 cc., add  $\text{BaCl}_2$  and boil, add pure milk of lime, boil and filter. Add  $(\text{NH}_4)_2\text{CO}_3$  and  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ , allow to settle and filter. Add  $\text{NH}_4\text{Cl}$  and a few drops of  $\text{HCl}$ , and evaporate to dryness. Ignite at a very low red heat, preferably in a closed vessel. A small portion of the mixed chlorides may be examined in the spectroscope, using a thin blue glass to counteract the effect of sodium and potassium, when, if lithium is present, the carmine red line *a* will appear equal in intensity to the potassium *a* if only a trifling amount of lithium is present.

If lithium is present it may be determined in the mixed chlorides by the method\* of Mr. F. A. Gooch, as follows: Take up the mixed chlorides as found above in the smallest quantity of water and boil with amyl alcohol, heating gently at first to avoid bumping, until the water disappearing from the solution and the point of ebullition rising and becoming

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\*Bulletin, U. S. Geol. Survey, No. 42, p. 73.

constant for some minutes, at a temperature which is about that at which the alcohol boils, the chlorides of sodium and potassium are deposited and lithium chloride is de-hydrated and taken into solution. Cool, add a few drops of HCl and again boil until the alcohol is free from water. If the amount of lithium chloride is small, it will now be in solution. If, however, the weight of lithium chloride exceeds 10 or 20 milligrams, it is advisable to decant the liquid from the residual chlorides of sodium and potassium, wash the latter with anhydrous amyl alcohol, dissolve in a few drops of water, and repeat the separation by another boiling with amyl alcohol. Filter, adding to the weight of the insoluble chlorides 0.00041 grams for every 10 cc. of amyl alcohol in the filtrate, exclusive of washings, if the insoluble salt is all sodium chloride; adding 0.00051 grams if all potassium chloride, or, adding 0.00092 grams if both chlorides are present. Evaporate the filtrate and washings to dryness, treat with  $H_2SO_4$ , drive off the excess of acid and ignite to fusion. Weigh as lithium sulphate, subtracting from this weight 0.00050 grams, 0.00059 grams or 0.000109 grams under the conditions mentioned above.

*Sodium and Potassium.*—It is frequently the case that the sodium is largely in excess of the potassium; if this be the case, or, if either element is present in relatively small amount, they are best determined as follows. Dissolve the weighed chlorides in the smallest quantity of water, add excess of a concentrated, neutral solution of  $PtCl_4$ , evaporate nearly to dryness on the water bath, add some 80 per cent. alcohol, allow to stand for some time, decant the liquor on a small filter, wash the residue several times in a similar manner with fresh portions of 80 per cent. alcohol. Wash the precipitate on the filter with 80 per cent..

alcohol, dry and transfer to a watch glass as far as possible. Dissolve the part adhering to the filter and evaporate to dryness in a weighed platinum dish, add the portion on the watch glass and dry to constant weight at 125° C., cool and weigh. This weight of  $K_2PtCl_6$  multiplied by 0.1941 gives the weight of  $K_2O$ . Calculate the KCl in the  $K_2PtCl_6$  by multiplying by 0.3071, and subtract this weight from the weight of the mixed chlorides. The remainder is the weight of NaCl, of which 53.07% is  $Na_2O$ .

If the sodium and potassium do not occur in widely different proportions, their relative amounts may be determined by calculation, as follows: Dissolve the mixed chlorides in water and titrate the chlorine with Reagents 30-a and 30-b. Multiply the weight of chlorine found by 2.1043, and subtract from this product the weight of the mixed chlorides. Multiply the remainder by 3.6358, and the product equals the weight of NaCl, according to the equations:—

$$x = 7.6511 C - 3.6358 S; \text{ or, } 3.6358 (2.1043 C - S).$$

$$y = 4.6358 (S - 1.6504 C);$$

in which x and y equal the weight of NaCl and KCl respectively, C equals the total chlorine found by titration, and S equals the weight of the mixed chlorides.

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*Determination of Sulphuretted Hydrogen.*—Measure 25 to 50 cc. of n/100 Iodine (Reagent 30-c) into a 500 cc. flask, and add the water to be examined until the color of the iodine disappears; add 5 cc. of starch indicator (Reagent 22), and add n/100 Iodine till the blue color appears. Fill the flask to the mark with distilled water, noting the amount used, and calculate the amount of water titrated by the amount of the standard iodine consumed.

*Determination of Five Carbonic Acid.*—Take 50 cc. of the water and add, without delay, 3 cc. of Reagent 30-l, 2 cc. of Reagent 30-e, and 45 cc. of Reagent 30-f. Cork the flask, shake and allow the precipitate to settle. Take out 25 cc. of the clear liquid by means of a pipette and titrate the remaining alkali with n/10 acid. The number of cc. of n/10 acid used are deducted from the number originally required for 45 cc. of the  $\text{Ba}(\text{OH})_2$  solution used, and the remainder, multiplied by 0.0022 will give the weight of  $\text{CO}_2$  existing free and as bicarbonate in the volume of water (50 cc.) used.

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*Determination of Boric Acid.*—The presence of boric acid may be detected by rendering one litre of the water alkaline with  $\text{Na}_2\text{CO}_3$ , evaporating to dryness, acidifying with HCl, moistening a piece of turmeric paper with the liquid and drying it. If boric acid is present the paper becomes a brownish-red color.

*Gooches Method.*—Render one litre of the water alkaline with  $\text{Na}_2\text{CO}_3$  and evaporate to dryness. Add a slight excess of acetic acid to the residue and transfer to the flask of a distilling apparatus arranged as follows:

A 250 cc. flask provided with a tubulation midway of its neck is fastened in the clamp of a ring-stand and closed with a perforated stopper containing a separatory funnel. Below the flask an open water-bath rests upon a ring of the stand, having sufficient range of vertical movement so that the bath may be alternately raised to enclose the flask and lowered away from it. The tubule of the flask is connected with a vertical condenser at whose lower extremity the terminal tube reaches nearly to the bottom of a 150 cc.

flask. About one gram of pure CaO is heated in a platinum crucible over the blast for fifteen minutes to decompose any hydrate or carbonate, cooled in a desiccator and weighed. It is then put into the condensing flask and slaked by addition of a few cc. of water and the flask attached to the lower end of the condenser; the tube from the condenser dipping into the solution of lime. The water bath, or vessel used, is filled with paraffin heated to about 120° C. and raised so as to immerse the flask above; the liquid in the flask is then distilled to dryness and the paraffin bath lowered. When the flask is sufficiently cool, 10 cc. of methyl alcohol are introduced through the funnel, the bath is raised and the liquid again distilled to dryness. Six portions of amyl alcohol, of 10 cc. each, are similarly distilled off. The boric acid will be distilled and fixed by the lime. Concentrate the contents of the lime flask and transfer completely to the crucible in which the lime was formerly heated and weighed, dissolving any portions adhering to flask or tube in acetic acid; cautiously dry the contents of the crucible and heat over the blast lamp for ten minutes. The increase in weight equals the boric acid.

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*Determination of Hardness.*—Waters containing considerable quantities of calcium and magnesium salts are said to be hard. Since the solution of the carbonates of calcium and magnesium in water depends partly upon the presence of carbon di-oxide, boiling precipitates the greater portion of the carbonates, the result being to diminish the hardness, or “soften” the water. Magnesium and calcium chlorides are not precipitated by boiling. Hardness, therefore, is divided into two classes, temporary and permanent; the former is

that which may be removed by boiling. Hehner's process is here given, as taken from Leffmann and Beam.

*Temporary Hardness.*—100 to 250 cc. of the water are tinted with lacmoid or phenacetolin indicator and heated to boiling, when standard  $H_2SO_4$  (Reagent 30-h) is cautiously run in until the color change occurs. Each cc. required will represent one part of calcium carbonate, or its equivalent, per 100,000 parts of water.

*Permanent Hardness.*—To 100 cc. of the water is added an amount of sodium carbonate solution (Reagent 30-g) more than sufficient to decompose the calcium and magnesium sulphates, chlorides and nitrates present; usually a bulk equal to the water taken will be more than sufficient. The mixture is evaporated to dryness in a platinum dish, and the residue extracted with distilled water. The solution is filtered through a very small filter, and the filtrate and washings titrated hot with standard  $H_2SO_4$ , as above; the difference between the number of cc. of standard  $Na_2CO_3$  used and the acid required for the residue will give the permanent hardness.

If the water contains sodium or potassium carbonate there will be no permanent hardness, and there will be more acid required for the filtrate than the equivalent of the sodium carbonate added. From this excess the quantity of sodium carbonate in the water may be determined.

Since any alkali carbonate in the water would be erroneously calculated as temporary hardness by the direct titration, the equivalent, in terms of calcium carbonate, of the alkali carbonate present should be deducted from the figure given by the titration in order to get the true temporary hardness.

The total  $CO_2$  in normal carbonates is given by the direct

titration of the water with dilute  $H_2SO_4$ . One cc. of the acid is equivalent to 0.0006 grams of  $CO_2$ .

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### *Concerning Water for Steam Boilers.\**

The main conditions affecting the value of a water for steam-making purposes are its tendency to cause corrosion and the formation of scale. Corrosion may be due to the water itself, to the presence of free acids, or to substances which form acids under the influence of the heat to which the water is subjected.

Pure water, or distilled water, exhibits a powerfully corrosive action upon iron. The dissolved oxygen which all waters contain also aids in corrosion, and especially when accompanied, as is usually the case, by carbonic acid. There is always greater rusting at the point at which the water enters the boiler, since there the gases are driven out of solution and immediately attack the metal. The corrosive action of oxygen and carbonic acid is especially noticeable in waters that are comparatively pure, such as those from mountain springs. Free acid, other than carbonic acid, is not often found in water, and if present renders the water unfit for use, unless it be neutralized. Mine waters are most likely to contain free acid, sulphuric acid being generally present. Magnesium chloride is frequently present in waters, and if in considerable quantity may be very harmful. At a temperature of  $310^{\circ} F.$  ( $160^{\circ} C.$ ), corresponding to an effective pressure of four atmospheres, it reacts with water to form magnesium oxide and hydrochloric acid, the latter attacking the boiler, especially at

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\*Leffmann and Beam.

the water line. If there is also present considerable calcium carbonate the evil may be somewhat lessened, but there may still be corrosion, so that the presence of more than a small quantity of the salt, say a grain or two to the gallon, may be considered objectionable. Allen has suggested the addition of sodium chloride in order to form with the magnesium salt the insoluble double salt.

Scale is composed of matters deposited from the water either by the decomposition induced by heat or by concentration. When the deposit is loose it is termed sludge, and usually consists of calcium carbonate, magnesium oxide and a small amount of magnesium carbonate. The formation of sludge is the least objectionable effect, since it may be readily removed by blowing off, provided that care is taken to allow the flues to cool down, so that when the water is removed the heat of the flues may not bake the deposit to a hard mass. Waters containing calcium sulphate form hard incrustations, difficult to remove and causing great loss of fuel by hindering the transmission of heat to the water. It not only forms a hard incrustation itself, but becomes incorporated with the mud and renders it hard also. The hard scale will also contain practically all the silica, iron and alumina in the water, beside any matter originally held in suspension.

Hence, a water only temporarily hard will, if care is taken in the management of the boiler, only cause the formation of a loose deposit of sludge; temporary hardness being mainly due to calcium and magnesium carbonates. A water permanently hard will probably form a hard scale, since such hardness is usually due to calcium sulphate.

The analysis of water for steam purposes, then, may include the determination of free acid, total solid residue,  $\text{SO}_4$ ,

Cl, Ca, Mg, temporary and permanent hardness. Where but small amounts of  $\text{SO}_4$  and Cl are present, the temporary and permanent hardness only need be determined.

Since calcium sulphate is practically insoluble in water above  $212^{\circ}$  F., the proportion of calcium sulphate may be regarded as such as would be formed by the total quantity of calcium or the total quantity of  $\text{SO}_4$ , whichever is present in larger quantity. Similarly, as the decomposition of magnesium chloride is induced by the high temperature of the boiler, the analysis should show the maximum amount of this salt obtainable from the magnesium and chlorine present. These rules cannot apply absolutely to waters rich in alkali carbonates, since these would neutralize any acid formed from the magnesium chloride, or even prevent its formation, and would prevent to a large extent the formation of calcium sulphate.

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### Analysis of Fertilizers.

Beside calcium phosphate and free phosphoric acid, superphosphates contain varying amounts of ferric phosphate, aluminum phosphate, calcium chloride and sulphate, nitrogenous matter, water and other impurities. The material is valued in commerce by the amounts of soluble, citrate-soluble, and citrate-insoluble phosphoric acid; the citrate-soluble consisting of the so-called "reverted" phosphoric acid, or  $\text{CaHPO}_4$ . The following arrangement of the methods of analysis is that adopted by the Association of Official Agricultural Chemists, November, 1898.

*Preparation of Sample.*—The sample should be well intermixed, finely ground, and passed through a sieve having circular perforations 1 mm. in diameter. The grinding and sifting should be performed as rapidly as possible, to avoid loss or gain of moisture during the operation.

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*Determination of Moisture.*—In potash salts, sodium nitrate and ammonium sulphate, heat from 1 to 5 grams at about 130° C. until the weight is constant. The loss in weight is considered as moisture. In all other fertilizers, heat 2 grams (or 5 grams if the sample be very coarse) for five hours, at 100° in a steam bath.

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*Total Phosphoric Acid.*—Treat 2 grams of the sample by one of the methods given below. After solution, cool, dilute to 200 or 250 cc., mix and pour on a dry filter.

- (1) Ignite and dissolve in hydrochloric acid.
- (2) Evaporate with 5 cc. of magnesium nitrate, ignite, and dissolve in hydrochloric acid.
- (3) Boil with from 20 to 30 cc. of strong sulphuric acid, adding from 2 to 4 grams of sodium or potassium nitrate at the beginning of the digestion and a small quantity after the solution has become nearly colorless, or adding the nitrate in small portions from time to time. A Kjeldahl flask marked at 250 cc. is recommended. After the solution is colorless, add 150 cc. of water and boil for a few minutes, cool, and make up to mark.
- (4) Digest with strong sulphuric acid and such other reagents as are used in either the plain or modified Kjeldahl or Gunning method for estimating nitrogen. Do not add

any potassium permanganate, but after the solution has become colorless add about 100 cc. of water and boil for a few minutes, cool, and make up to a convenient volume; 2.5 grams of substance and a digestion flask marked at 250 cc. are recommended.

(5) Dissolve in 30 cc. of concentrated nitric acid and a small quantity of hydrochloric acid, and boil until organic matter is destroyed.

(6) Add 30 cc. of concentrated hydrochloric acid, heat, and add cautiously, in small quantities at a time, about 0.500 grams of finely pulverized potassium chlorate, to destroy organic matter.

(7) Dissolve in from 15 to 30 cc. of strong hydrochloric acid and from 3 to 10 cc. of nitric acid. This method is recommended for fertilizers containing much iron or aluminum phosphate.

*Determination.*—Take an aliquot portion of the solution prepared by one of the methods given above, corresponding to 0.25 gram, 0.50 gram, or 1 gram, neutralize with ammonia, and clear with a few drops of nitric acid. In case hydrochloric or sulphuric acid has been used as a solvent, add about 15 grams of dry ammonium nitrate, or a solution containing that amount. To the hot solution add 50 cc. of molybdic solution (Reagent 32-b) for every decigram of  $P_2O_5$  that is present. Digest at about 65° C. for an hour, filter, and wash with cold water, or preferably ammonium nitrate solution (Reagent 32-c). Test the filtrate for phosphoric acid by renewed digestion and addition of more molybdic solution. Dissolve the precipitate on the filter with ammonia and hot water, and wash into a beaker to a bulk of not more than 100 cc. Nearly neutralize with hydrochloric acid, cool, and add magnesia mixture (Reagent 32-d)

from a burette; add slowly (about 1 drop per second), stirring vigorously. After fifteen minutes add 30 cc. of ammonia solution of density 0.96. Let stand for some time; two hours is usually enough. Filter, wash with 2.5 per cent.  $\text{NH}_3$  (Reagent 32-e) until practically free from chlorides, ignite to whiteness or to a grayish white, and weigh.

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*Water-Soluble Phosphoric Acid.*—Place 2 grams of the sample on a 9 cm. filter, wash with successive small portions of water, allowing each portion to pass through before adding more, until the filtrate measures about 250 cc. If the filtrate be turbid, add a little nitric acid. Make up to any convenient definite volume; mix well, take an aliquot part, and proceed as under total phosphoric acid.

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*Citrate-Insoluble Phosphoric Acid.*—In acidulated samples, heat 100 cc. of strictly neutral ammonium citrate solution of 1.09 specific gravity (Reagent 32-a) to 65° C. in a flask placed in a bath of warm water, keeping the flask loosely stoppered to prevent evaporation. When the citrate solution in the flask has reached 65° C., drop into it the filter containing the washed residue from the water-soluble phosphoric acid determination, stopper tightly with a smooth rubber, and shake violently until the filter paper is reduced to a pulp. Place the flask in the bath and maintain it at such a temperature that the contents of the flask will stand at exactly 65° C. Shake the flask every five minutes. At the expiration of exactly thirty minutes from the time the filter and residue are introduced, remove the flask from the bath and immediately filter the contents as rapidly as possible. Wash thoroughly

with water at 65° C. Transfer the filter and its contents to a crucible, ignite until all organic matter is destroyed, add from 10 to 15 cc. of strong hydrochloric acid, and digest until all phosphate is dissolved; or, return the filter with contents to the digestion flask, add from 30 to 35 cc. strong nitric acid, from 5 to 10 cc. strong hydrochloric acid, and boil until all phosphate is dissolved. Dilute the solution to 200 cc. If desired, the filter and its contents may be treated according to methods (2), (3), or (4), under total phosphoric acid. Mix well; filter through a dry filter; take a definite portion of the filtrate and proceed as under total phosphoric acid.

In non-acidulated samples, in case a determination of citrate-insoluble phosphoric acid is required, it is to be made by treating 2 grams of the phosphatic material, without previous washing with water, precisely in the way above described, except that in case the substance contains much animal matter (bone, fish, etc.) the residue insoluble in ammonium citrate is to be treated by one of the processes described under total phosphoric acid (2), (3), or (4).

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*Citrate-Soluble Phosphoric Acid.*—The sum of the water-soluble and citrate-insoluble, subtracted from the total, gives the citrate-soluble phosphoric acid.

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*Sodium and Potassium.*—Take 50 cc. from original solution, under water-soluble acid, remove bases and determine alkalies according to the method given under Water Analysis.

*Hydrochloric Acid*.—Take 50 cc. of same solution, boil, and precipitate third group with  $\text{NH}_4\text{OH}$  and filter. If the filtrate is still strongly colored with organic material, add  $\text{KNO}_3$  and evaporate the solution to dryness in a platinum dish; ignite well, cool, take up with  $\text{HNO}_3$  and water, filter. Titrate the filtrate with standard  $\text{AgNO}_3$ , as under Water Analysis.

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*Sulphuric Acid*.—Take another 50 cc., acidify with  $\text{HCl}$ , boil, filter, and precipitate by addition of boiling solution of  $\text{BaCl}_2$ , as elsewhere directed.

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*Calcium and Magnesium*.—Take another 50 cc., boil and add excess of  $\text{NH}_4\text{OH}$ , boil, filter and wash. Precipitate calcium and magnesium in the filtrate as usual.

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#### **Analysis of Clays, Feldspars, Kaolin and Fire Sands.**

Finely pulverize and dry the sample at  $100^\circ \text{ C}.$ ; fuse 1 gram, with 10 grams of  $\text{Na}_2\text{CO}_3$  and a very little  $\text{KNO}_3$ , cool and thoroughly disintegrate the fusion with hot water. Transfer to a platinum dish, acidulate with  $\text{HCl}$  and evaporate to dryness on the water bath. Heat in the air-bath for one-half hour at  $100^\circ$  to  $104^\circ \text{ C}.$  Treat again with  $\text{HCl}$  and water, evaporate to dryness, and again heat for one-half hour as before. Take up with  $\text{HCl}$  and water, filter, wash, dry, ignite, cool and weigh the residue. Moisten with water, add a few drops of  $\text{H}_2\text{SO}_4$  and treat with HF; evaporate to dryness, ignite, cool and weigh. The loss in weight is  $\text{SiO}_2$ . If there is any appreciable residue, dis-

solve it in HCl or (better) fuse with KHSO<sub>4</sub>, take up and add to filtrate from the silica. Heat the solution to boiling in a platinum dish, add excess of NH<sub>4</sub>OH, boil till the NH<sub>4</sub>OH is almost driven off, filter and wash thoroughly with hot water. Reserve the filtrate. Dissolve the precipitate on the filter in dilute HCl, and wash thoroughly, receiving the filtrate in a platinum dish. Reserve the filter paper. Precipitate again with NH<sub>4</sub>OH as before, filter and wash thoroughly until the washings give no precipitate with AgNO<sub>3</sub> when acidulated; add the filtrate and first washings to the reserved filtrate. Dry the precipitate and remove it from the filter. Incinerate the reserved filter paper in a platinum crucible, add the last filter paper and incinerate carefully at a low heat; add the precipitate and raise the heat gradually to a dull red. Cool and weigh as Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub>. Fuse this residue with KHSO<sub>4</sub>, dissolve in cold water, dilute to 500 cc. and titrate the iron and titanium as under Analysis of Titanic Iron Ores. Determine the alumina by difference.

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*Calcium and Magnesium.*—Evaporate the above filtrate to dryness in a platinum dish, with the addition of strong HNO<sub>3</sub> to destroy ammonium salts. Take up in water, filter if necessary, add a little HCl and a slight excess of NH<sub>4</sub>OH; add a solution of 1 gram of (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and let stand till the precipitate is settled. Filter, wash, dry and ignite to CaO.

Concentrate the filtrate to small bulk, add excess of NH<sub>4</sub>OH, make thoroughly cold, add Na<sub>2</sub>HPO<sub>4</sub> with stirring, and let stand over night. On filtering, decant as much as possible onto the filter and throw away the filtrate; dissolve

the precipitate with a few drops of HCl and water, pour the solution on the filter and wash with a very small quantity of water. Make the filtrate alkaline with NH<sub>4</sub>OH and shake. Let stand one hour, filter and wash. Dry, ignite. to Mg<sub>2</sub>P<sub>2</sub>O<sub>7</sub>, cool and weigh.

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*Sodium and Potassium.*—See Insoluble Silicates.

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### Fuller's Earth.

This substance is an earthy, hydrated silicate of alumina, whose constituents may be determined according to the method last given. It is thus named on account of its former use by fullers, for removing grease and oil from cloth. It is now largely used for bleaching cotton-seed oil and for clarifying crude petroleum and lubricating oils. Its chemical composition varies; but any substance supposed to be fuller's earth may be conveniently tested by its efficiency in the functions last mentioned above, and may be analyzed according to methods given for similar substances.

*By Bleaching Cotton-Seed Oil.*—Take 100 grams of the yellow cotton-seed oil, and place in a beaker. Heat on the water-bath to 170° or 180° F., and add about 8 grains of the fuller's earth which has been ground to 120-mesh. Stir frequently with a glass rod for about twenty minutes, still heating on the water-bath; then filter through a fluted filter. With the English earth, the oil should come through the filter colorless.

*By Clarifying Oils.*—Grind the earth to about 8-mesh, and fill up a burette with it. Pour the oil in at the top, and

let it filter through. If the earth is of good grade, the oil should come through *not* colorless, but clear.

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### Potassium and Sodium in Insoluble Silicates.

Mix 0.500 grams of the finely pulverized silicate with the same quantity of  $\text{NH}_4\text{Cl}$  in an agate mortar; add four grams of  $\text{CaCO}_3$  and further mix. Transfer the charge to a platinum crucible, cover and ignite gently for a few minutes, to decompose the  $\text{NH}_4\text{Cl}$ , then apply a bright red heat for about one hour. Cool the crucible, place it in an evaporating dish, add water and heat; remove the crucible, washing it thoroughly, and digest the mass to complete disintegration. Filter and wash well; to the filtrate add some  $(\text{NH}_4)_2\text{CO}_3$  and a few drops of  $\text{NH}_4\text{OH}$  and concentrate to about 50 cc., add a little more  $(\text{NH}_4)_2\text{CO}_3$  and a few drops of  $\text{NH}_4\text{OH}$  and filter. To the filtrate add a few drops of  $(\text{NH}_4)_2\text{CO}_3$  and concentrate; if a precipitate is formed, filter it off; repeat the operation till no further precipitate is formed, then evaporate to dryness in a weighed platinum dish, and heat carefully to faint redness. The residue consists of the mixed chlorides of sodium and potassium; cool and weigh. Separate the sodium and potassium, or estimate indirectly, according to the methods given under Water Analysis.

**Analysis of Metallic Aluminum.\***

*Iron.* (a).—Dissolve from 1 to 5 grams in HCl. Proceed as with an iron ore, titrating with standard  $K_2Cr_2O_7$ , or

(b) Decompose 3 grams of chips in a 500 cc. flask with 50 cc. of a 40 per cent. solution of KOH; when dissolved, add 200 cc. of  $H_2SO_4$  (sp. gr. 1.16) and boil to a clear solution. Titrate with standard  $KMnO_4$ .

*Silicon and Silica.*—Dissolve 1 gram in aqua regia. Evaporate to dryness, take up with 5 cc. of strong HCl, add water, boil and filter. Wash with dilute HCl and weigh as Si and  $SiO_2$ . Fuse with  $Na_2CO_3$  and determine the total silica.

*Copper and Lead.*—Dilute the filtrate from the silica until the free HCl is only about 1 per cent. of the solution. Pass  $H_2S$  gas through the solution while boiling and filter. Dissolve the residue in  $HNO_3$  (sp. gr. 1.20) and filter off the sulphur. Add 5 cc. of  $H_2SO_4$  and evaporate till fumes of  $SO_3$  are given off. Dilute and, after waiting some time, filter off lead sulphate, from which estimate the lead. Nearly neutralize the filtrate with  $NH_4OH$  and precipitate the copper by the battery.

*Aluminum.*—Receive the filtrate from the copper and lead in a 500 cc. flask, and dilute to 500 cc. Take about 50 cc. (equals 0.100 grams of metal), boil off the free  $H_2S$ , oxidize the iron with bromine, and precipitate the Fe, Al, etc., with  $NH_4OH$ . Ignite and weigh. Subtract the weight of the iron and the result equals the alumina plus the phosphorus.

*Lime and Magnesia.*—Determine in the filtrate from the last operation.

*Alkalies.*—Dissolve 1 gram in HCl and separate the silica.

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\*Jour. of Analyt. and Appl. Chem.

Oxidize the iron and precipitate the iron and aluminum with  $\text{NH}_4\text{OH}$ . After washing, dissolve this residue in  $\text{HNO}_3$  and evaporate in a platinum dish to dryness on the water bath. Heat over the flame till the  $\text{Al}_2(\text{NO}_3)_6$  is all decomposed, the residue is white and friable, and no acid fumes are indicated by  $\text{NH}_4\text{OH}$ . Exhaust with hot water, to get the alkaline nitrates into solution and unite the filtrate with that from the iron precipitation. Evaporate and separate the lime and magnesia, then weigh the alkalies as chlorides.

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#### *Analysis of Mineral Phosphates.*

*Moisture.*—Two grams of the substance are very carefully weighed in accurately-tared and well-ground watch-glasses; the latter are then adjusted with the clip so as to leave a sufficient opening for the passage of steam, and placed in the drying-oven at  $110^\circ \text{ C}$ . for three hours, then cooled and weighed. The loss equals the moisture.

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*Combined Water and Organic Matter.*—The residue from the last operation is carefully brushed into an accurately-tared platinum crucible, which is placed over a small Bunsen flame for ten minutes, and then brought to a white heat in the blast; after so heating for five minutes, the crucible is covered, cooled and weighed. The loss in weight includes combined water, organic matter and  $\text{CO}_2$ , the latter of which must be deducted from the weight found after having been determined as follows:

*Carbonic Anhydride*.—This is determined by treatment of 2 grams of the original substance in Schroetter's Apparatus, which may be purchased of any dealer in chemical supplies.

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*Insoluble Siliceous Matter*.—Place 5 grams of the original sample in a casserole with about 30 cc. of aqua regia, cover with an inverted funnel, place on the sand bath, heat gradually and finally evaporate to dryness. Cool, moisten with strong HCl, evaporate to dryness and heat ten minutes at 125° C. Cool, allow to digest for fifteen minutes with 50 cc. of strong HCl, dilute with water, filter and wash with hot water till filtrate measures 250 cc., dry, ignite and weigh.

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*Sulphuric Anhydride*.—Twenty-five cc. of the last filtrate, representing 0.500 grams of the phosphate, are placed in a beaker, boiled, and treated while boiling with 5 cc. of a saturated solution of BaCl<sub>2</sub>. The hot liquid is filtered and the residue thoroughly washed with boiling water, dried, ignited and weighed.

*Phosphoric Anhydride*.—Twenty-five cc. of the filtrate from the siliceous matter, representing 0.500 grams of the phosphate, are placed in a beaker with 10 grams of NH<sub>4</sub>NO<sub>3</sub>. The solution is heated and when quite warm is treated with 150 cc. of molybdate solution (Reagent 6) and well stirred; after digesting at 70° C. for one hour it is filtered and the residue well washed with water. Place the beaker in which the precipitation was made under the funnel, pierce the filter with a stirring rod, and wash the precipitate into the beaker

with a hot, 20 per cent. solution of  $\text{NH}_4\text{OH}$ ; the bulk of the filtrate should not exceed 75 cc.

Nearly neutralize the filtrate with HCl until the yellow color only disappears with difficulty; cool and add, drop by drop, 20 cc. of magnesia mixture (Reagent 3), stirring constantly with a glass rod. Add about 50 cc. of strong  $\text{NH}_4\text{OH}$ , stir again and allow to stand for four hours. Filter, wash, dry and ignite with the usual precautions, and weigh the pyro-phosphate.

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*Fluorine*.—To determine the presence of fluorine, place 2 or 3 grams of the phosphate in a platinum dish with about 2 cc. of  $\text{H}_2\text{SO}_4$ . Cover the dish with a watch-glass thinly coated with wax, through which some mark has been traced with a needle-point. Gently heat for ten minutes, remove the glass and wash off the wax. If an etching appears, fluorine is present.

Fuse 5 grams of the phosphate in a platinum dish with 15 grams of the mixed carbonates of sodium and potassium and 2 grams of very fine sand, using a very strong heat for fifteen minutes. Cool, dissolve in water, and treat with excess of  $(\text{NH}_4)_2\text{CO}_3$ , to remove all soluble silica; filter and wash with great care; nearly neutralize the filtrate with HCl and treat with an excess of  $\text{CaCl}_2$  solution.

The precipitate, consisting of phosphate, fluoride and some carbonate of lime, is washed several times by decantation with boiling water, filtered, washed, dried and ignited. After cooling, treat the residue with acetic acid and evaporate to dryness on the water-bath, to form calcium acetate of all the calcium carbonate. Wash out the residue with boil-

ing water, filter, dry, ignite and weigh. The weight represents the calcium phosphate and fluoride in the sample.

Return the residue to a platinum dish, add 5 cc. of strong  $H_2SO_4$  and drive off the fluorine by heat. Cool and treat with 100 cc. of alcohol, filter and wash with alcohol up to 200 cc.

The alcoholic filtrate contains the phosphoric acid, and this is precipitated with magnesia mixture, as usual, washed, dried, ignited and weighed. Figure the  $P_2O_5$  as calcium phosphate and subtract it from the combined weights of phosphate and fluoride of calcium obtained by the acetate treatment, thus obtaining the calcium fluoride by difference. From this calculate the fluorine.

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*Oxides of Iron and Alumina.*—There is a penalty for any excess of these oxides present in phosphate rock, over 3 per cent.; consequently great care is necessary in their determination.

This highly-important determination is, however, a matter of some difficulty. The method herein given is recommended by Dr. Wyatt, as being sufficiently accurate, rapid and economical.

Fifty cc. of the filtrate from the siliceous matter, equaling 1 gram of the phosphate, are placed in a beaker and made alkaline with  $NH_4OH$ . The resulting precipitate is re-dissolved by the addition of just sufficient  $HCl$ , and the liquid is then again made alkaline with  $NH_4OH$  in very slight excess. Fifty cc. of concentrated and pure acetic acid are now added; the mixture is stirred and allowed to stand in a cool place *until perfectly cold*. It is then filtered on an

ashless filter and the beaker and residue are carefully washed twice with boiling water. The flask containing the filtrate is then removed from beneath the funnel and replaced by the beaker in which the first precipitation was made. The substance on the filter is now carefully dissolved in a little hot 50 per cent. solution of HCl, and the filter is washed twice with hot water. The filtrate in the beaker is next made alkaline with NH<sub>4</sub>OH in slight excess; then made strongly acid with pure concentrated acetic acid, well stirred up, and again allowed to stand till absolutely cold. The flask containing the first filtrate is now replaced under the funnel, the liquid in the beaker is filtered into it, the filter is washed twice with cold water containing a little acetic acid, and three times with boiling distilled water.

The funnel containing the filter is now placed in the oven and completely dried, after which the filter and its contents are calcined and weighed as *phosphates of iron and alumina in one gram of the material.*

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When reporting upon a sample for commercial purposes, that is to say, when determining its value to the manufacturer of water-soluble super-phosphates, it is sometimes necessary to carry this analysis a little further. In such cases, after carefully noting the accurate weight of the combined phosphates, they are dissolved in boiling HCl. The solution is filtered into a 100 cc. flask and washed up to the mark with boiling water. No residue should remain on the filter, save perhaps a speck or two of carbon resulting from the recent incineration. In one-half of the filtrate the phosphoric anhydride is determined by the molybdate method

already described. The remaining half of the filtrate is boiled with a small piece of zinc in a flask fitted with a Bunsen valve. When the iron is completely reduced and gives no trace of pink coloration with KCNS, the liquid is cooled, about one gram of magnesium sulphate is dissolved in it, and it is then titrated with n/100 KMnO<sub>4</sub>, every cc. of which equals 0.000799 grams of ferric oxide. Add together the total phosphoric anhydride and ferric oxide determined in the last operation, and subtract their sum from the weight of the combined phosphates of iron and alumina previously determined, thus getting the alumina by difference.

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*Lime.*—The total filtrates from the iron and alumina determination first described are mixed by shaking the flask, and are then concentrated by boiling down to about 100 cc. At this point there are added to the liquid about 20 cc. of a saturated solution of (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, and the mixture, after stirring, is withdrawn from the fire, covered with a watch-glass and allowed to stand for six hours. At the end of this time the supernatant fluid is filtered through an ashless filter; the residue is washed three times by decantation with boiling water, filtered, and washed at least three times more. Dry, ignite at a low heat for ten minutes, then with the blast for five minutes, cover, cool, and weigh as CaO.

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*Magnesia.*—The filtrates and all of the washings from the lime determination, as above detailed, are well shaken together, and boiled down to about 100 cc. Make thoroughly cold, pour into a beaker, and make strongly alkaline with NH<sub>4</sub>OH. Add Na<sub>2</sub>HPO<sub>4</sub> and, after well stirring, cover

with a watch-glass and allow to stand over night. Filter, wash with dilute  $\text{NH}_4\text{OH}$ , dry, and ignite to  $\text{Mg}_2\text{P}_2\text{O}_7$ .

The details for the above methods for the analysis of mineral phosphates are taken from Dr. Wyatt's comprehensive treatise, *The Phosphates of America*.

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### Analysis of Smelting Ores.

Owing to the wide variety of metals which such ores may contain, it may be considered somewhat unsafe to prescribe a general method for complete analysis. With this fact in mind, however, the following can be made useful in many cases; especially if particular determinations are checked by examination of separate samples, as given later on.

*Portion for Silica, Lead, Lime and Magnesia.*—Take 1 gram of the sample, previously pulverized and dried at 100° C., dissolve in a casserole in aqua regia, and evaporate to dryness. Moisten thoroughly with HCl, take up in hot water, filter and wash with hot water. Reserve the filtrate. Pierce the filter, wash the residue into a beaker with excess of hot water, and boil; decant the greater part of the liquid on a filter, add to the residue an excess of  $\text{NH}_4\text{Cl}$  solution, and boil to remove silver and lead; decant this liquid on the filter, add more water to residue and boil again; filter and wash. Unite the filtrates above and reserve. If barium is present in the ore, it will be found, in part at least, in the above residue. Dry the residue, ignite, cool and weigh. Treat in the crucible with  $\text{H}_2\text{SO}_4$  and HF, evaporate to dryness, cool and weigh again. The loss in weight is due to silica.

Make the reserved filtrate alkaline with  $\text{NH}_4\text{OH}$ , stir and let settle; if no blue color appears, there is not over 0.3 per cent. of copper. Whether copper is present or not, add 10 to

20 cc. of fresh, yellow ammonium sulphide, free from carbonic acid, until the whole solution looks yellow after mixing and settling. Let stand in a flask, corked, for 15 minutes; filter rapidly and wash with water containing ammonium sulphide. Reject the precipitate. Acidify the filtrate with HCl, boil hard for one hour, or evaporate to one-half bulk, and filter off antimony sulphide and free sulphur. Wash the precipitate with water containing some hydro-sulphuric acid, place it with filter in a stoppered flask, and digest at a gentle heat with a saturated solution of  $HgCl_2$  in HCl (sp. gr. 1.12) until the precipitate is white. Add water till not less than one-sixth of the volume of the solution is strong HCl, add excess of standard  $K_2Cr_2O_7$  and titrate back with standard solution of  $FeSO_4$ . N/10 factor for antimony = 0.003005.

The precipitated sulphides above may also contain arsenic and tin; in which case the mixed sulphides should be dissolved in  $NH_4OH$ , and oxidized in this solution by the action of chlorine gas or bromine. Remove traces of the oxidizing agent by boiling, add tartaric acid, a large quantity of  $NH_4Cl$  and an excess of ammonia. If there is a precipitate, more  $NH_4Cl$  or tartaric acid must be added till it dissolves. Concentrate the solution as much as possible, precipitate with magnesia mixture (Reagent 3) in alkaline solution, and let stand 3 hours; filter, wash with dilute  $NH_4OH$ , dry at 105° C. and weigh as  $MgNH_4AsO_4$  on a previously weighed filter; otherwise, after drying, ignite and weigh as  $Mg_2As_2O_7$ . Acidify the filtrate from the arsenic with HCl, and precipitate antimony and tin with  $H_2S$  gas. Dissolve 20 grams of oxalic acid in 200 cc. of hot water; dissolve the mixed sulphides in ammonium sulphide, add to the above solution, dilute to 400 cc., heat nearly to boiling and pass into it  $H_2S$  gas for one-half hour. The precipitate contains all of the antimony, but also a small amount of tin. Filter quickly, dissolve the precipitate in ammonium sulphide, and pour into a boiling, concentrated solution of oxalic acid, passing  $H_2S$  gas while the solution boils. Filter off antimony sulphide, and determine antimony as above. Unite filtrates, make alkaline with ammonia, add ammonium sulphide, acidify with acetic acid, filter and wash with solution of ammonium acetate acidified with acetic acid, dry, remove most of precipitate and ignite filter alone; moisten with  $HNO_3$ , evaporate to

dryness and ignite; now add precipitate, cover the crucible, ignite gently, finally with full heat, till all sulphur is burnt off and the residue exists as stannic oxide. In order to remove the last traces of  $H_2SO_4$  the ignition may be repeated with addition of a little  $(NH_4)_2CO_3$ , then cool and weigh.

Thallium and indium, if present, will be found in the ammonium sulphide precipitate.

To the filtrate add excess of  $NH_4OH$ , boil, filter if necessary, add a solution of ammonium oxalate and boil for five minutes. Allow to settle, filter and wash by decantation with hot water; in this wet precipitate determine the lime by the volumetric method given under Analysis of Limestone. In the filtrate determine the magnesia as usual.

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*Portion for Arsenic.*—Treat a separate portion of the ore by the following method. It is rapid and fairly accurate, but is not so nearly exact as Method (2) which follows. Antimony is conveniently separated, but phosphoric and molybdic acids, if present, interfere.

Place 0.500 grams in a platinum crucible. If the substance to be analyzed consists of arsено-pyrite, or contains a large amount of arsenic, add a few drops of strong  $HNO_3$  and digest, afterward proceeding by the general method, as follows: Fuse with from six to ten parts of a mixture of equal parts of  $Na_2CO_3$  and  $KNO_3$ , commencing with a low heat and gradually increasing to perfect fusion; cool and take up in boiling water. Filter, acidulate with  $HNO_3$  and boil to expel  $CO_2$  and nitrous fumes. Cool, dilute with water to a certain volume, take duplicate portions for check analyses, and treat each portion as follows: Add an excess of  $ZnO$  emulsion (Reagent 16) and mix thoroughly, leaving an ex-

cess of ZnO in the beaker. In some cases filtration is necessary at this point if much silica or alumina is present. Add an excess of AgNO<sub>3</sub> solution, mix thoroughly, and make a further addition of ZnO emulsion; mix, filter and wash with cold water. Dissolve the residue of silver arseniate and ZnO on the filter in hot, dilute HNO<sub>3</sub>, cool, add a few drops of ferric nitrate and titrate the silver with n/10 NH<sub>4</sub>SCN. Each cc. is equivalent to 0.010793 grams of silver, which corresponds to 0.0025 grams of arsenic.

*Method (2).*—This method is offered by the authors\* as giving better results than the one above. Larger samples of ore can be conveniently handled. If molybdic acid is present, the results obtained for antimony are apt to be somewhat high.

To 1 gram of the prepared sample add 10 cc. of strong nitric acid in a 3-inch casserole, and warm. When red fumes have nearly ceased, add about 10 cc. of strong sulphuric acid and evaporate till copious fumes of the latter arise. Do not boil too long beyond this point, or small amounts of arsenic may be volatilized. Cool, and add 40 cc. of cold water and 10 cc. of hydrochloric acid; also some tartaric acid, if antimony is to be determined. Boil to dissolve all soluble matter. If much gangue is present, filter; if not, wash into a No. 3 Griffin beaker with warm water, and reduce to a colorless solution by addition of a mixture of one part ammonium bisulphite and two parts strong ammonia. The reducing agent should be added drop by drop with constant stirring, waiting for the precipitate formed to be re-dissolved after each addition. Only sufficient of the reagent should be used to decolorize the solution. In case the hydrates formed do not

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\*Skinner & Hawley, E. & M. Jour., lxxiv, 5.

dissolve, add a little more hydrochloric acid. Gold, selenium and tellurium, if present, will be reduced and will darken the solution; hence, after they are precipitated no more sulphite need be used. Boil the solution till there is no apparent odor of sulphurous acid, and while still warm introduce a rapid current of hydrogen sulphide; continuing for about fifteen minutes, or until the precipitated particles gather together and the supernatant liquid is no longer murky. Filter though an 11 cm. paper, washing the sulphides onto the paper with water. Wash out iron salts thoroughly, and test filtrate with hydrogen sulphide.

Introduce the filter and sulphides into a 4-ounce distillation flask whose arm is bent downward and connected with a Liebig condenser, set vertically. If necessary to wash the sulphides into the flask, use the smallest adequate portion of hydrochloric acid of sp. gr. 1.10.

When filter and contents are in the flask, introduce, through a funnel reaching well into the flask, 50 cc. of cupric chloride solution (Reagent 37-a). A thermometer is passed through the stopper to within about one-fourth inch of the bottom of the flask, the flask is placed on a sand-bath which is sufficiently wide to prevent the flame from reaching the sides of the flask, and the outlet of the condenser is placed about one-half inch below the surface of about 40 cc. of cold water in a No. 1 beaker. The flask and contents are gradually heated till the thermometer reads about 115° C.; the beaker containing the distillate is removed, another for the purpose of collecting a second distillate is put in place, the stopper of the distilling flask is removed and 10 to 25 cc. of strong hydrochloric acid are introduced, and the distillation repeated; it is not necessary, however, if only small

amounts of arsenic are present. The distillates are made alkaline with ammonia, then they are just acidified with hydrochloric acid, cooled, about 2 grams of sodium bi-carbonate and some starch solution are added, and the arsenious acid titrated with standard iodine (Reagent 37-b).

The distilling flask is then fitted with a tube, reaching nearly to the bottom of the flask and connected with a generator of hydrochloric acid. The generator contains hydrochloric acid of sp. gr. 1.20, into which sulphuric acid of sp. gr. 1.84 is allowed to drop at the rate of about two drops per second. Another beaker containing cold water is placed below the condenser, and the flask is heated till the contents become about dry. The heating should not be carried too far, since copper chloride is apt to come over. To the distillate in the beaker add a little tartaric acid, almost neutralize with ammonia and precipitate antimony, if present, with hydrogen sulphide. If antimony is found, the distillation should be continued as before till no more is found in the distillate. The sulphide of antimony is filtered through a Gooch crucible, heated in the air-bath for one hour at 255° C., cooled and weighed. The result, multiplied by 71.42 will give the weight of antimony.

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*Portion for Lead, Copper, Iron and Zinc.*—Treat 1 gram of the ore with  $\text{HNO}_3$  in a beaker, boil till red fumes no longer arise, cool slightly, add 5 cc. of  $\text{H}_2\text{SO}_4$  and evaporate to moist dryness. Cool, dilute with 150 cc. of water, add a little salt to precipitate silver, boil, settle fifteen minutes and filter, washing with 1%  $\text{H}_2\text{SO}_4$ . Dissolve the lead sulphate in the residue in hot solution of ammonium acetate, and determine the lead as in Method (2) below.

To the filtrate, containing copper, iron, zinc, etc., add a few drops of  $H_2SO_4$ , boil and precipitate copper with sodium thio-sulphate, according to the method given under Analysis of Brass. The copper sulphide may then be dissolved, and the copper determined by one of the methods given under Analysis of Copper Ores and Products.

To the filtrate from the copper add HCl and a few crystals of  $KClO_3$ , and boil hard till the chlorine is expelled. Nearly neutralize with ammonia, add ammonium chloride and cool. Add a few drops of bromine and 20 cc. of ammonia, boil and let settle for fifteen minutes. Filter off the precipitate of iron, alumina, manganese, etc., and, if considerable in size, dissolve in HCl, re-precipitate in the same manner, wash with hot water and reserve. Concentrate the clear filtrate to small volume, acidify with HCl, and determine the zinc by titration with ferro-cyanide, according to the method given below. Dissolve the reserved residue in HCl and determine the iron by titration with standard  $K_2Cr_2O_7$ .

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*Determination of Sulphur.*—Place 0.500 grams of the ore in a flask with 3 grams of  $KClO_3$  and heat with occasional additions of  $HNO_3$  till about 10 cc. have been added. Boil and evaporate off the excess of acid. The sulphides should be decomposed and there should be no free sulphur. Add 30 cc. of water and an excess of a saturated solution of  $Na_2CO_3$  and boil for one hour, adding water as the solution boils down. Filter through a ribbed filter and wash till the washings show no trace of  $H_2SO_4$ . Acidify the filtrate, boil off  $CO_2$  and precipitate with  $BaCl_2$  as usual. As the above filtrate is apt to contain some silica, it should first be evaporated to dryness, cooled, taken up in HCl and water, and

filtered; after which the precipitation with  $\text{BaCl}_2$  may be made.

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*Determination of Alumina.*—After the solution of the ore and separation of the insoluble residue, second group metals are removed by precipitation with  $\text{H}_2\text{S}$  and filtration, the filtrate is boiled to expel  $\text{H}_2\text{S}$ , and a few drops of  $\text{HNO}_3$  are added to oxidize iron. Proceed from this point according to the method given under Analysis of Iron Ores.

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*Determination of Barium.*—Dissolve 0.500 grams of the ore according to one of the preceding methods; when it is probable that a large part of the barium will remain with the insoluble residue, while another part is dissolved. Reserve the filtrate, dry the insoluble residue and fuse with sodium carbonate, pour, and dissolve in water with boiling; discard the filtrate from the fusion, wash the residue thoroughly with water, and dissolve in  $\text{HCl}$ ; add to the reserved filtrate, boil, add sufficient  $\text{NH}_4\text{OH}$  to precipitate iron, etc., add sufficient  $\text{H}_2\text{SO}_4$  to precipitate barium, dissolve the iron precipitate by addition of  $\text{HCl}$ , cool and filter, washing by decantation with water containing 10% of  $\text{HCl}$ . Dry, ignite, treat with  $\text{H}_2\text{SO}_4$  and  $\text{HF}$  to remove silica, cool and weigh.

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*Determination of Manganese.*—Decompose 0.500 grams of the ore with 2 cc. of strong  $\text{HNO}_3$ , 3 cc. of dilute  $\text{H}_2\text{SO}_4$ , and 6 cc. of strong  $\text{HCl}$ , and evaporate to dryness in a casserole. Cool, add 20 cc. of water and boil; nearly neutralize with a saturated solution of sodium carbonate, and, if too much is

added, correct with dilute sulphuric acid. Add to the solution an excess of basic carbonate of lead suspended in water (prepared by adding a hot solution of lead acetate to a hot solution of sodium carbonate as long as a precipitate is formed, filtering, and washing thoroughly to remove sodium salts), and stir vigorously. Heat to boiling without filtration, and titrate with standard solution of  $\text{KMnO}_4$ , stirring after each addition of the reagent. Each cc. of the permanganate solution equals 0.5 per cent. of manganese in the weight taken, and is made by dissolving 4.792 grams of permanganate in one litre of water.

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*Determination of Lead.—Method (1). (By Mr. A. H. Low.)*—Provide three wash-bottles for the following solutions:—(1) Distilled water, free from chlorine; (2) dilute sulphuric acid (one part of acid to nine of water) free from chlorine; (3) a saturated solution of ammonium chloride. Treat 1 gram of the ore, in a beaker, with 10 cc. of pure, strong  $\text{HNO}_3$  and 10 cc. of pure, strong  $\text{H}_2\text{SO}_4$ . Heat until all of the nitric acid is expelled and the sulphuric acid boils freely; cool and add 10 cc. of the dilute sulphuric acid above-mentioned. Add 2 grams of Rochelle salts and, when this is dissolved, add 40 cc. of water. Boil and allow to settle two minutes; filter and wash with the dilute sulphuric acid. Dissolve the residue on the filter (or in a beaker if there is much gangue) with hot, saturated solution of  $\text{NH}_4\text{Cl}$  above; filter and wash. In the solution containing the lead, place a strip of aluminum foil, boil five minutes and wash by decantation. Press the lead into a sheet with an agate pestle, wash with alcohol, dry, holding the dish in the hand, and weigh as metallic lead.

*Method (2).* (By Mr. H. H. Alexander.)—If the substance contains less than 30% of lead, take 1 gram; if it contains 30% or over, take one-half gram, boil down in a casserole with 15 cc. of strong  $\text{HNO}_3$  and 10 cc. of strong  $\text{H}_2\text{SO}_4$  till  $\text{SO}_3$  fumes arise; cool, dilute with cold water, and mix to thorough solution. Decant as thoroughly as possible onto a filter, leaving the residue in the casserole. Wash the filter twice with hot, dilute  $\text{H}_2\text{SO}_4$  and once with cold water. Throw away the filtrate. Dissolve the lead sulphate in the residue in hot solution of ammonium acetate, by repeated additions, and filter; washing the casserole thoroughly with hot water. Dilute the filtrate to 250 cc. with hot water, boil and titrate with standard molybdate solution (Reagent 33-a) till all of the lead is precipitated and a drop of the solution, tested with tannin solution (Reagent 33-b), on a porcelain slab, shows no yellow color. Antimony, arsenic and phosphorus do not interfere.

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*Method (3).* (By Mr. H. A. Guess.)\*

The methods given under this head are modern and cover the subject of the determination of lead very satisfactorily. Two methods are given; one being applicable to all ores and not being affected by the presence of commonly-occurring elements; the other being simply a modified or shortened form of the first, and applicable to all ores except when antimony is present, or a considerable amount of bismuth or silver; it is especially adapted to the determination of lead in heavy lime ores.

Both methods are based upon the quantitative precipitation of lead from its acetate solution by either normal or acid potassium chromate in standard solution. The lead chromate is filtered off, the filtrate acidified with  $\text{HCl}$ , a small amount of potassium iodide is added, this reacts with the excess of chromic acid in the filtrate

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\*Trans. Am. Inst. Mining Engineers—Sept., 1904.

and iodine is set free; the iodine liberated is then titrated with standard sodium thio-sulphate as usual. If antimony is not present, the residue containing the lead chromate may be treated with hot dilute HCl, filtered, washed with hot water, and the chromic acid in the filtrate determined as above. From the equation between  $K_2CrO_4$  and  $Pb(C_6H_5O_2)_2$  it will be found that 9.3958 grams of the former reagent will precipitate 10 grams of lead; or, if a standard solution of  $K_2CrO_4$  be made, containing 9.3958 grams per litre, each cc. thereof will precipitate 0.010 grams of lead. Further, from the equations between  $K_2CrO_4$  and KI and between the liberated iodine and sodium thio-sulphate, it will be found that, if a solution of thio-sulphate be made containing 35.2721 grams per litre, each cc. thereof will be equivalent to 1 cc. of the potassium chromate standard. The writer suggests that one-half the above strength solution of thio-sulphate is more desirable.

The sample is treated according to the manipulations given under the molybdate method (Method 2); the filter containing the lead sulphate is returned to the original flask, slightly acid ammonium acetate is added, and the mixture digested a few minutes, until the lead sulphate is completely dissolved. Antimony, if present, affects the complete solution of the lead at this point; the difficulty is overcome by using slightly ammoniacal ammonium acetate to off-set the acid nature of the antimony residue, and by prolonging the digestion of the filter and contents; after dilution, the solution should be slightly acidified with acetic acid before precipitation with the chromate. In adding the standard chromate solution it is desirable, if the lead content be approximately known, to add only a few cc. of chromate in excess, in order to minimize the washing or back-titration. The filtration may be made directly after adding the chromate solution, using a close-grained, 11 cm. paper; the lint present in the flask from the original sulphate filter will serve to check any tendency of the lead chromate to pass through. The bulky residues from large ore-charges are

difficult to wash; consequently, the use of a slight excess of chromate solution, and the back-titration of such excess is considered preferable to direct solution and titration of the lead chromate precipitated. When only about 1 per cent. of lead is present in the sample, and it is desired to make the back-titration directly after adding the chromate, it is necessary to keep the bulk of the strong ammonium acetate solution used within 10 cc. and to dilute with cold water to a bulk not exceeding 50 cc. before adding the chromate.

The following short-cut method is devised for heavy lime ores:—Treat from 1 to 5 grams of ore in a 250 cc. flask with from 3 to 5 cc. of strong  $\text{HNO}_3$  and 15 cc. of strong  $\text{HCl}$ ; digest to complete solution and the excess of acid has been reduced to about 8 cc. Remove flask from heat and slowly add slightly dilute ammonia in slight excess. Then add slowly 80% acetic acid, shaking vigorously, till the smell indicates an excess. Then add 5 cc. of strong ammonium acetate to insure solution of any lead compounds. If the ore contains no antimony, or separated gelatinous silica, and if the siliceous residue in the bottom of the flask is only in slight amount (as is usual with heavy lime ores or with concentrates), add to the hot, undiluted and unfiltered solution an excess—about 10 cc.—of a 10% chromate solution. Under these conditions the contents of the flask will not exceed 50 cc. After shaking and allowing to settle for five minutes, filter through a rapid and close filter, and the lead chromate will be granular and show no tendency to run through. Wash the residue several times with hot water containing about 0.5 per cent. of acetic acid until free from soluble chromates. The funnel with its filter is then set over the original flask, and hot, dilute  $\text{HCl}$  (1 to 1) is poured through the filter

to complete the solution of the lead chromate; then wash thoroughly with hot water. Add to the filtrate a small crystal of KI (from 0.500 to 2 grams in weight) and titrate with standard sodium thio-sulphate, the most suitable strength for which is 1 cc. equal to 0.005 grams of lead. In this operation, by using only a small quantity of KI and having the solution fairly strong with HCl (about 50 cc. HCl of half strength in 200 cc. of solution) and somewhat warm, any tendency of the lead to form yellow scales of PbI<sub>2</sub> is completely checked, and the end reaction is clear.

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### *Determination of Zinc.*

In describing the following method, the author, Mr. A. H. Low, states that the method is not of universal application; sometimes a fusion may be necessary to effect complete decomposition of the ore, or perhaps a preliminary treatment with hydrochloric acid may be necessary, in which case all the acid must be carefully expelled before beginning the regular treatment. The operator is expected to recognize such cases and apply the remedy; being careful, however, not to modify the method except from actual necessity.

Place 0.500 grams of the ore in a 250 cc. pear-shaped flask, add about 2 grams of KNO<sub>3</sub> and 5 cc. of strong HNO<sub>3</sub>; heat until the acid is about half gone, add 10 cc. of a cold saturated solution of KClO<sub>3</sub> in strong HNO<sub>3</sub>, and boil to complete dryness. It is usually necessary to manipulate the flask in a holder, over a naked flame, to avoid loss by bumping. The boiling may be conducted rapidly, and toward the end it is best to heat the entire flask, so as to expel every trace of liquid. The KNO<sub>3</sub> serves simply as a diluent of the dry residues, and insures the completeness of the subsequent extraction of the zinc. Cool sufficiently and add 30 cc. of a prepared ammonia solution (Reagent 31-a) and heat

to boiling. Boil very gently for about two minutes, filter through a 9 cm. filter, and wash with a hot solution of  $\text{NH}_4\text{Cl}$  containing about 100 grams of the salt and 50 cc. of strong ammonia to the litre. Collect the filtrate in a 400 cc. beaker. The insoluble residue should be completely disintegrated, and any ferric hydrate present should appear of a fine, sandy nature. Place a bit of litmus paper in the filtrate (not necessary if much copper is present) and neutralize carefully with  $\text{HCl}$ , finally adding 6 cc. of the strong acid in excess. Dilute to about 150 cc. and add 50 cc. of a cold saturated solution of  $\text{H}_2\text{S}$ . Heat nearly to boiling and the solution is ready for titration. If more convenient, or apparently advisable, pass a current of  $\text{H}_2\text{S}$  gas through the hot solution diluted to 200 cc. Copper and cadmium, which are interfering metals, are thus precipitated; unless in large amount, they need not be filtered off. Practically no zinc is precipitated with the copper under these conditions, and the discoloration of the liquid by even 10% of copper does not badly mask the uranium test. Titrate the hot solution as follows:—Pour off about one-third, and set it aside in a beaker. Titrate the remainder, more or less rapidly, according to the amount of zinc indicated, with the standard ferro-cyanide solution (Reagent 31-b), until the end point is passed, using the uranium indicator. Now add the greater part of the reserved portion, and continue the titration with more caution until the end-point is again passed. Finally, add the last of the reserved portion, and finish the titration carefully, ordinarily two drops at a time. Make corrections for the final reading of the burette, precisely as in the standardization. The true end-point is always slightly passed, and, after waiting a minute, it is usually sufficient to deduct

for as many drops as show a brown tinge and one test additional. (See Waring's method under Analysis of Zinc Ores.)

NOTE.—When precipitating with  $H_2S$  it is a matter of considerable importance to have the solution of a definite degree of acidity. Cadmium and copper are to be precipitated, while it is better to retain lead in solution and not unnecessarily blacken the liquid with its sulphide. If there is enough acid to prevent the precipitation of its sulphide, the lead will not interfere in the titration. On the other hand, too much acid will prevent the precipitation of the cadmium. It will not come down from a boiling hot solution containing 5% of strong HCl, but is readily precipitated from a 3% solution, while lead is not, if the liquid be nearly boiling. It is therefore recommended to have an excess of 6 cc. of strong HCl in the final volume of 200 cc. of solution.

Arsenic, when present in large amount, sometimes makes trouble by retaining iron in the ammoniacal solution. No attention need be paid to arsenic unless its presence in excess is thus indicated. In such case, begin anew, giving the ore a preliminary treatment as follows: To 0.500 grams of ore in the flask add 10 cc. of strong HCl and 1 cc. of bromine. Warm very gently for several minutes, to decompose the ore without loss of bromine, and then boil rapidly to complete dryness. The arsenic will thus be sufficiently expelled. Now add  $KNO_3$  and  $HNO_3$  and proceed in the usual manner.

In the case of ores that are free from cadmium, or where cadmium may be neglected, the copper may be readily precipitated without the use of  $H_2S$ , as follows: After neutralizing the ammoniacal filtrate from the insoluble residue, acidify with an excess of 10 cc. of HCl and add about 30 grams of granulated test lead. Heat nearly to boiling, and stir the lead about until all the copper is precipitated. Now dilute to 200 cc. and titrate as described, without removing the lead and precipitated copper.

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*Determination of Cadmium.*—See Waring's method, under Analysis of Zinc Ores.

*Determination of Mercury.*

The following method\* is especially adapted for low-grade ores, but can be applied to others by reducing the size of the sample or by increasing the capacity of the apparatus used. It is not only quantitative, but will also serve as a rapid qualitative test.

Mix from 0.100 to 2 grams of the sample with from 1 to 4 grams of iron filings, in a porcelain crucible of proper size. Arrange a cover for the crucible, made of sheet gold, and so constructed that it may be dish-shaped on top and may have an over-hanging gutter, so that cold water may be applied for the purpose of condensing the fumes of mercury. Weigh the gold cover, fill with water, and adjust to crucible; carefully heat the crucible, endeavoring to keep the upper part and cover cool, and replacing the water when necessary. In from 10 to 30 minutes the distillation will be complete, the cover may be removed, carefully dried and weighed; the increased weight being due to the mercury.

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*Analysis of Lead Slags.*

The silver is usually determined by fire assay, thus leaving  $\text{SiO}_2$ ,  $\text{CaO}$ ,  $\text{FeO}$  and  $\text{Pb}$  as the more important remaining ingredients, with occasional necessity for the estimation of  $\text{ZnO}$ ,  $\text{MnO}$ ,  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{BaO}$ , etc.

In case the sample of slag has been chilled, its decomposition by acid is usually easy; if, however, the sample has been allowed to cool slowly, a fusion will probably be necessary. This should be made either with  $\text{Na}_2\text{CO}_3$  in a porcelain crucible, since lead might injure platinum, or the sample may be mixed with  $\text{Na}_2\text{CO}_3$  and heated, *not to fusion*, in a

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\*Eschka. Zeitschrift fur analytische Chemie., II, 344.

platinum or porcelain dish, the heating being performed in a muffle. After such heating the slag should be soluble in acid.

*Portion for SiO<sub>2</sub>, FeO, Al<sub>2</sub>O<sub>3</sub>, CaO, and MgO.*—Take of the finely pulverized, chilled slag 0.500 grams and treat with water and strong HCl, with constant stirring, following the method for the decomposition of Blast Furnace Slag. Add a little HNO<sub>3</sub> to oxidize iron and any sulphides, and a few drops of H<sub>2</sub>SO<sub>4</sub>, and evaporate to dryness. Cool, moisten with HCl and take up with water; filter by decantation. Before bringing the residue on the filter, treat it with 10 cc. of a hot, saturated solution of NH<sub>4</sub>Cl, to dissolve lead salts; filter, wash, dry, ignite and weigh the SiO<sub>2</sub>.

If barium is present it will, in the above case, be retained and weighed with the silica. It may be separated from this residue by one or more fusions with Na<sub>2</sub>CO<sub>3</sub> and leachings with hot water; finally dissolving the BaCO<sub>3</sub> formed in HCl and precipitating with H<sub>2</sub>SO<sub>4</sub>. In the filtrate from the silica, the iron, alumina, etc., may be precipitated with NH<sub>4</sub>OH, washed, dried, ignited and weighed, after which they may be fused with Na<sub>2</sub>CO<sub>3</sub>, dissolved in HCl and water, and both iron and alumina directly determined if desired, as under Analysis of Iron Ores.

In the filtrate from the iron and alumina the CaO and MgO may be determined as usual.

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*Portion for Lead.*—Decompose from 1 to 5 grams of the slag as before, and proceed according to Low's method. See Analysis of Smelting Ores.

*Portion for Manganese.*—Decompose 1 gram of the slag with water, HCl, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> as before, and evaporate till SO<sub>3</sub> fumes come off heavily. Take up with boiling water, nearly neutralize with Na<sub>2</sub>CO<sub>3</sub>, precipitate the iron with ZnO (Reagent 16) and proceed by Volhard's Method, under Analysis of Iron and Steel.

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For Zinc, Sulphur and other metals see Analysis of Smelting Ores, and Analysis of Zinc Ores.

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### Analysis of Copper Ores and Products.

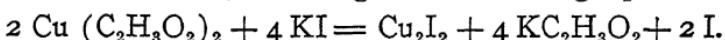
*Determination of Copper, Method (1).*—A. H. Low's modification\* of Beringer's Method.†—Treat 0.500 grams of the ore in a flask of 250 cc. capacity, with 5 or 6 cc. of strong HNO<sub>3</sub>, and boil gently nearly to dryness. Add 5 cc. of strong HCl and again boil; as soon as the incrusted matter is dissolved, add 5 cc. of strong H<sub>2</sub>SO<sub>4</sub> and heat strongly; best by manipulating the flask in a holder over a small, naked flame, until the more volatile acids are expelled, and fumes of sulphuric acid come off freely. Allow to cool, then add 20 cc. of cold water and heat to boiling, to thoroughly dissolve anhydrous sulphates of iron, etc. Filter, (more especially to remove any lead sulphate) and receive the filtrate in a beaker about two and one-half inches in diameter. Wash the flask and filter with hot water, keeping the volume down to about 50 or 60 cc. Place in the beaker two pieces of sheet aluminum, of about one-sixteenth of an inch in thickness,

\*Journal Am. Chem. Soc., XVIII, 5, page 458.

†C. and J. J. Beringer. Text-book of Assaying, page 159.

and about one and one-half inches square, with alternate corners bent up and down. Add 5 cc. of strong  $H_2SO_4$ , cover the beaker, heat to boiling, and boil strongly for about seven minutes. Unless the bulk of the solution is excessive, this time will be sufficient for all amounts of copper. If the copper should adhere to the aluminum, it can usually be removed by a little additional boiling, or by use of a glass rod. Transfer the solution back to the original flask, rinsing in with the wash-bottle as much as possible of the copper, leaving the aluminum behind. Drain the beaker as completely as possible, and temporarily set aside, together with the aluminum, which may yet retain a little copper. Allow the copper in the flask to settle, and then decant the liquid through a filter. Again wash the copper two or three times with a little hot water, retaining the copper as completely as possible in the flask. Finally, wash the filter once or twice, endeavoring to wash all of the metallic particles down into the point. Pour upon the aluminum in the beaker 5 cc. of a mixture of equal volumes of strong  $HNO_3$  and water, and warm gently; do not heat to boiling, as the aluminum would be unnecessarily attacked. See that any copper present is dissolved, and pour the warm solution through the filter last used, thus dissolving any contained particles of copper, and receive the filtrate in the flask containing the main portion of the copper. Do not wash either the aluminum or the filter, but simply remove the flask, and set the beaker in its place. Boil the mixture in the flask till all of the copper is dissolved, then add about one-half gram of potassium chlorate, and again boil for a minute,—to oxidize any arsenic present. Remove the flask from the lamp, place it under the funnel, and wash the beaker, aluminum and filter with the smallest

adequate quantity of hot water. Boil sufficiently to remove all traces of red fumes. All of the copper is now in the flask, as nitrate. Add about 20 cc. of a cold saturated solution of zinc acetate, heat to boiling, cool to ordinary temperature, and dilute to about 50 cc. Add about 3 grams of KI and shake gently till dissolved. Cuprous iodide will be precipitated and iodine liberated, according to the following equation:—



The free iodine colors the mixture brown. Titrate at once with standard sodium thio-sulphate until the brown tinge becomes weak; then add starch liquor to produce marked blue color, and cautiously continue the titration until the blue color is entirely gone. When almost at the end, allow a little time for reaction after addition of each drop. One cc. of the standard thio-sulphate equals 0.005 grams of copper; hence, if a half gram sample is taken, each cc. of thio-sulphate equals 1 per cent. copper.

The solution of sodium thio-sulphate is prepared as follows:—Prepare a solution containing 19.123 grams of pure crystals of the salt in 1 litre. Accurately weigh about 0.200 grams of pure copper foil, place in a 250 cc. flask, add 5 cc. of a mixture of equal volumes of strong  $\text{HNO}_3$  and water, and thoroughly boil off red fumes,—a very essential point. Remove the lamp, add zinc acetate and titrate as above, making the thio-sulphate solution of a strength in which 1 cc. equals 0.005 grams of copper.

The starch liquor is made by boiling about one-half gram of starch in a little water, and diluting with hot water to about 250 cc. It is used cold, and must be prepared frequently, as it will not keep.

Silver does not interfere with this method. Arsenic, when

oxidized as described, has no influence. Lead and bismuth are without effect, except that their iodides may mask the end-point, before adding starch.

*Method (2). Titration with Potassium Cyanide.\**—One gram of the finely pulverized ore is placed in a flat-bottomed 250 cc. flask, or in a casserole; 7 cc. of  $\text{HNO}_3$  and 5 cc. of  $\text{H}_2\text{SO}_4$  are added and boiled down till the  $\text{HNO}_3$  is expelled. Cool and add 6 grams of commercial sheet zinc cut into small strips, shake and allow to stand five minutes, add 50 cc. of water and 20 cc. of  $\text{H}_2\text{SO}_4$ . When the zinc is all dissolved, fill the flask with water, allow it to settle, decant the clear supernatant liquid and test it for copper. Fill the flask with water, settle and decant twice. To the residue add 5 cc. of strong  $\text{HNO}_3$  and boil to expel nitrous fumes, add one drop of strong  $\text{HCl}$  and, if much silver is indicated, add one drop more, dilute with a little water and filter. To the filtrate add 10 cc. of strong  $\text{NH}_4\text{OH}$ , cool and add about 125 cc. of water.

If the color of the solution indicates only a small amount of copper, filter and titrate the filtrate; if considerable copper is present, titrate without filtration with standard KCN (Reagent 34) until the blue color becomes faint, then filter and finish the titration. At the latter part of the operation the solution should measure about 180 cc., being brought to this bulk by dilution if necessary; the standard KCN should be added drop by drop and the flask shaken after each addition. When the tint desired by the operator is observed (such tint as he considers the end reaction when standardizing the KCN solution with pure copper), the operation is finished.

With ores containing much arsenic, the zinc should be

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\*A. H. Low's Modification, Proceedings Col. Sci. Soc., Vol. I.

allowed to react on the solution for from ten to fifteen minutes before it is dissolved in  $H_2SO_4$ ; after the solution the first decantation should be made quickly.

*Method (3). By Electrolysis.—*

In nitric acid solutions, preferably containing free  $H_2SO_4$ , copper is separated by electrolysis from iron, aluminum, chromium, cobalt, nickel, zinc, and cadmium. From silver, mercury and bismuth copper cannot be separated in presence of  $HNO_3$  or  $H_2SO_4$ . From a solution of copper and lead, containing 5 per cent. of  $HNO_3$ , the copper is completely precipitated at the cathode, and the lead as di-oxide, at the anode. Copper is separated from manganese in solutions containing an excess of  $H_2SO_4$ . In dealing with solutions where (beside copper), arsenic, antimony, or tin is present, the metals are precipitated as sulphides, the sulphides treated with  $Na_2S$ , with heat if necessary, the insoluble sulphide of copper is removed and treated separately. In the electrolysis of copper solutions,  $HCl$  should never be present.

While the electrolytic estimation of copper furnishes an elegant method, under favorable conditions, it will be noticed that various metals seriously interfere, unless removed by chemical manipulation of the original solution of the ore or alloy; and for general technical use, except in cases where the copper is to be determined in substances of fairly constant or simple composition, the preference is generally given to other methods, notably Methods (1) or (2).

*Operation.—*Take an amount of the pulverized ore in which there shall not be over 0.250 grams of copper, dissolve, treat with metallic zinc, wash the precipitated copper by decantation, etc., as in Method (2). Dissolve the copper in a small quantity of strong  $HNO_3$  with boiling, add 5 cc. of  $H_2SO_4$  and evaporate till most of the  $HNO_3$  is gone; cool, dilute slightly and filter into a beaker, when the solution should measure about 100 cc.

A convenient apparatus for precipitation is that used by Luckow,\* in which the cathode consists of a cylinder of

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\*Crookes, p. 323, also Smith's Electro-Chem. Anal., p. 53.

platinum foil which dips into the solution to be electrolyzed, and the anode consists of a spiral of stout platinum wire, so wound as to appear like a watch-spring, the interior end of the wire being prolonged to establish connection with the battery. The anode rests on the bottom of the beaker, about one-eighth of an inch below the edge of the cathode. Or, the precipitation may be made in a platinum dish resting on a wire spiral connected with the negative pole of the battery, with an anode consisting of a piece of platinum foil dipping into the copper solution with which the dish is filled.

The cathode is cleaned, freed from grease by treatment with an alkali, dried and weighed. Connection is then made with the battery, for which the ordinary Crowfoot cell with a zinc, a copper and a solution of  $\text{CuSO}_4$  is cheap and efficient, furnishing a current of low intensity, but which is quite constant for a long period; or the Bunsen or Leclanche cell may be used. After connection has been made with the battery (the cylinder or dish with the zinc, and the spiral or foil with the copper), if the current does not seem to be sufficiently rapid, a few drops of strong  $\text{HNO}_3$  may be added to the copper solution. The precipitation requires, under varying conditions, from three to ten hours; when it is complete, the acid solution is siphoned from the beaker or platinum dish without interrupting the current (otherwise copper might be dissolved), replacing the acid liquid as it is siphoned off by pouring in pure water. When most of the acid has been removed, disconnect the apparatus, wash the precipitated copper with hot water, then with alcohol, dry at  $100^\circ \text{ C}.$ , cool in a desiccator and weigh. If silver is present in the substance treated, it will vitiate the result unless previously removed by  $\text{HCl}$ , which should itself be then removed.

In the treatment of the ordinary copper ores or products, where injurious metals, such as arsenic, antimony and bismuth, are not present, the solution may be made as usual, filtered and electrolyzed without the precipitation with zinc.

*Method (4).—The Thio-cyanate-Iodide Method.\**

This method is offered by the author to supersede the usual form of iodide assay for copper (wherein the copper is precipitated by metallic aluminum) in order to save time in the determination, to avoid loss by spattering in evaporation, and to avoid introduction of iron into the assay.

*Assay of Ore, Concentrates or Matte.*—Take such a sample as will contain from 0.100 to 0.240 grams of copper; place in a beaker, sprinkle over it about 2 grams of granulated potassium chlorate, add 10 cc. of strong nitric acid and cover the beaker immediately. Allow to stand for a short time, then rotate the beaker gently till violent action ceases. Heat gently till fumes of nitric oxide and chlorine are completely expelled, allow to cool and add 10 cc. of hydrochloric acid of sp. gr. 1.20, keeping the beaker covered as closely as possible; heat again and boil for a minute or two. If properly done, all of the sulphur will be oxidized, all of the copper will be in solution, and the residue will be clean and white. For ordinary work, this need not be filtered off. Cool, dilute with 50 cc. of cold water, add ammonia in excess, then barely acidify with dilute sulphuric acid. Heat to a point just below boiling, being careful that the solution is nearly neutral, add 10 cc. of sulphurous acid and stir, adding more sulphurous acid till the iron is completely reduced. Precipitate the copper with 5 cc. of ammonium thio-cyanate (Reagent 38-a). Stir, allow to settle for one minute, filter and wash with hot

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\*Andrew M. Fairlie, E. & M. Jour., LXXVIII, 20, 787.

water. Most of the precipitate will be on the filter, while some will remain in the beaker and on the stirring-rod; dissolve this residue with a few drops of nitric acid, wash the sides of the beaker with about 10 cc. of water, transfer precipitate and filter to the beaker, add 2 cc. of strong nitric acid and cover. Warm till the copper salt is dissolved, and boil gently till red fumes are gone. Remove the filter-paper, wash, and add washings to the contents of the beaker. Add ammonia to very slight but distinct alkalinity (since a large excess of ammonium acetate prevents complete reaction between copper acetate and potassium iodide), boil, acidify with acetic acid and cool. When cold, add 6 cc. of potassium iodide solution, mix the contents of the flask by agitation, and run in from a burette sufficient sodium thio-sulphate (Reagent 38-b) to almost destroy the brown color of the liberated iodine. Add 2 to 3 cc. of starch solution (Reagent 38-c), and continue the titration to a cream color. The thio-sulphate having been standardized against pure copper, each cc. will have a known value.

#### *Copper Mattes and Bullion.*

In these substances and in some rich copper ores the determination of the copper does not present the difficulty attaching to the determination of their contained silver and gold. These metals are generally determined by fire assay, but the presence of much copper renders the fire assay tedious and inaccurate also, unless special modifications are adopted; hence chemists have resorted to a more convenient procedure, by use of a combined wet and dry method, of which a convenient form is that proposed by Professor C. Whitehead,\* which is as follows:

Dissolve from one to four assay-tons of the matte or borings, in a No. 5 beaker, by the gradual addition of strong

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\*Jour. Anal. and App'd Chem., Vol. 6, page 262.

$\text{HNO}_3$ , expel nitrous fumes by boiling, add 50 cc. of a saturated solution of lead acetate and mix thoroughly, add 1 cc. of dilute  $\text{H}_2\text{SO}_4$  and allow the lead sulphate to settle, carrying with it the fine gold which may be suspended in the solution. Filter, wash with cold water, dry, incinerate the filter, scorify the whole with lead, cupel and part the resulting bead for gold.

To determine the silver, dilute the filtrate from the last operation to 1,000 cc. and divide in halves, making duplicate or check determinations as follows: Add to each portion a saturated solution of  $\text{NaBr}$  until a precipitate ceases to form. Filter the precipitated bromides of lead and silver, wash out the copper with cold water, dry, smelt each precipitate and its filter-ash in a small crucible, and cupel the resulting lead button for silver.

### *Copper Slags.*

The solution and analysis of copper slags may be made after the same manner as that given for lead slags. (See Analysis of Lead Slags.) In smelter practice, rapid determinations of copper in slags are made by the following colorimetric method:—

For chilled samples, take 1 gram, in a  $2\frac{1}{2}$ -inch casserole, add 10 cc. of water and 15 cc. of  $\text{HCl}$ ; heat to solution, add 15 cc. of  $\text{HNO}_3$  and boil, with cover on, till fumes disappear; wash into a 200 cc. flask, add 20 cc. of  $\text{NH}_4\text{OH}$ , and dilute to mark; shake well and filter, through a 15 cm. paper and corrugated funnel, into an 100 cc. Nessler tube. Compare with a known amount of standard copper nitrate solution, in another Nessler tube which is exactly similar to the first tube, placing both tubes over a porcelain plate for comparison. The standard copper nitrate solution is examined

electrically for copper. If the slag is not chilled, fusion with  $\text{Na}_2\text{CO}_3$  will be necessary to insure solution.

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*Determination of  $\text{Cu}_2\text{O}$  in Refined Copper.*—If 1 gram of the copper is digested, in the cold, with a solution of from 5 to 6 grams of  $\text{AgNO}_3$  in 100 cc. of water, until complete decomposition, two-thirds of the cuprous oxide will be precipitated as a basic nitrate of copper, according to the equation:  $3 \text{Cu}_2\text{O} + 6 \text{AgNO}_3 + 3 \text{H}_2\text{O} = 2 \text{Cu}(\text{NO}_3)_2 + 2 \text{Cu}_2\text{NO}_3(\text{OH})_3 + 6 \text{Ag}$ .

The residue is washed, dissolved in dilute  $\text{HNO}_3$ , silver is precipitated with  $\text{HCl}$ , and the copper determined in the filtrate. The copper found, multiplied by 1.6885, equals the weight of cuprous oxide.

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#### Analysis of Alloys, Brasses and Bronzes.

*Determination of Tin and Lead.*—Take 1 gram of the alloy in a 12-ounce beaker, add 15 cc. of  $\text{HNO}_3$  (sp. gr. 1.42) and evaporate to a condition just short of dryness, the residue being moist. Add 5 cc. of  $\text{HNO}_3$  (sp. gr. 1.42) and 30 cc. of water, and heat ten minutes; filter (returning turbid filtrates) and wash with water containing 1 per cent.  $\text{HNO}_3$ . Dry, ignite, cool and weigh as  $\text{SnO}_2$ . To the filtrate add 15 cc. of  $\text{H}_2\text{SO}_4$  (sp. gr. 1.84) and let stand two or three hours. (The small amount of  $\text{HNO}_3$  does not affect the  $\text{PbSO}_4$  if excess of  $\text{H}_2\text{SO}_4$  is present.) Filter, wash with a limited amount of water, using a weighed filter-paper which has been previously dried at  $100^\circ \text{C}$ . and its weight taken at the end of one minute. Dry the precipitate at  $100^\circ \text{C}$ . and weigh at

the end of one minute. This weight, less the weight of the filter, equals lead sulphate.

*Determination of Copper.*—Take 0.250 grams, add 5 cc. of HNO<sub>3</sub> (sp. gr. 1.42) and heat till dissolved and all red fumes are gone; add 15 cc. of water and 6 grams of zinc acetate and boil, add 50 cc. of water, cool, add 4 grams of potassium iodide and titrate with standard Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, according to Method (1) under Analysis of Copper Ores and Products.

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*Determination of Zinc.*—Treat 2 grams of the alloy with 20 cc. of HCl and enough HNO<sub>3</sub> (sp. gr. 1.42) to dissolve. Evaporate to dryness twice with HCl, to expel HNO<sub>3</sub>; dissolve the residue in 15 cc. of HCl, dilute with water to 300 or 350 cc., warm slightly, and pass H<sub>2</sub>S gas, with occasional stirring, till copper is all precipitated. Filter through a 12½ cm. paper, testing first portions of filtrate for copper with H<sub>2</sub>S. In filtering, keep the paper full, wash with water containing H<sub>2</sub>S, and do not allow the filter to stand empty; let it just drain after each addition of wash-water, then fill again. Wash six or seven times. Concentrate the filtrate to 150 or 200 cc. in a 6-inch dish; transfer to a pint beaker, boil, add solid Na<sub>2</sub>CO<sub>3</sub> almost to neutrality. Boil again, and slowly add Na<sub>2</sub>CO<sub>3</sub> solution till ZnCO<sub>3</sub> is precipitated; then add moderate excess of Na<sub>2</sub>CO<sub>3</sub>. Filter on an ashless paper and wash thoroughly with hot water. Dry, remove residue to a weighed porcelain crucible, and ignite filter strongly with blast. If iron is visible in this residue, dissolve the whole in HCl, precipitate the iron with NH<sub>4</sub>OH, filter, wash, dry, ignite, weigh and deduct from weight of ZnO.

In Phosphorus Bronzes, all of the  $P_2O_5$  is separated with the tin, if there be sufficient tin present to unite with it. In this case the phosphorus may be determined by dissolving the residue in strong aqua regia and proceeding as follows:— Cool, dilute slightly, filter off any crystals of lead chloride which may appear, and add molybdate solution to filtrate. Filter, wash with water containing 1 per cent  $HNO_3$ , and determine the phosphorus in the yellow precipitate by one of the methods previously given. To determine the tin, deduct the weight of phosphorus from the weight of the original residue.

If antimony is present, it is also to be found in the tin residue. To determine it, fuse the mixed tin and antimony oxides in a porcelain crucible with 6 to 8 grams of *dried*  $Na_2S_2O_3$ , for one-half hour, using blast. Dissolve the fusion in water and, if antimony is found to be present, as a precaution, fuse the residue in the same manner a second time. Take up with water, filter. Treat the residue with 15 cc. of  $HCl$  (sp. gr. 1.20), warm, and gradually raise the heat; add small portions of  $KClO_3$  till sulphur is gone or collected in a lump and the tin and antimony are dissolved, boil a few minutes and filter. In the filtrate, neutralize the  $HCl$  with  $KOH$  until a *permanent* turbidity forms, add about 15 grams of oxalic acid, dilute to 300 cc., boil, and while hot pass  $H_2S$  gas (Clarke's separation). Filter off  $Sb_2S_3$  on a weighed filter, wash, dry, wash with  $CS_2$ , dry and weigh; or, the precipitate may be dissolved in acid, the sulphur oxidized to  $H_2SO_4$  and precipitated with  $BaCl_2$ , and the antimony determined from the sulphur thus found.

In the analysis of Nickel Anodes, take 2 grams, dissolve in aqua regia and evaporate to dryness; add HCl and evaporate to dryness a second time. Cool, moisten with 5 cc. of HCl and take up with water; filter on weighed filter, wash, dry and weigh; ignite completely, cool and weigh again. The loss in weight is due to carbon. The second weight will give the silica. Pass H<sub>2</sub>S through the filtrate, precipitating tin and copper; filter, wash with water containing H<sub>2</sub>S and a little HCl; separate the tin by dissolving out with sodium sulphide and precipitating the resulting solution with HCl; filter, wash, ignite and weigh as SnO<sub>2</sub>. The sulphide of copper remaining on the filter may be determined electrolytically, or by the iodine method as elsewhere given. Boil the filtrate to expel the bulk of the H<sub>2</sub>S, add 5 cc. of HNO<sub>3</sub> (sp. gr. 1.40) and boil one minute more; pour the boiling solution into a mixture of 75 cc. of water and 25 cc. of strong NH<sub>4</sub>OH. If iron is present, repeat the above precipitation twice. Reduce the combined filtrates to 100 cc. in volume, add 1 cc. of NH<sub>4</sub>OH, then add 10 cc. of a solution of K<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (50 grams of the salt dissolved in 500 cc. of water), 5 cc. of KI solution (2.5 grams of KI to 100 cc. of water) and 10 cc. of AgNO<sub>3</sub> solution (1.33 grams of the salt in 1000 cc. of water), and titrate with standard KCN, according to the method given for the determination of nickel in nickel steel.

(Mr. Textor says that, if the K<sub>2</sub>C<sub>2</sub>O<sub>4</sub> above is omitted after removal of the iron, the KCN throws down nickel and re-dissolves it at the close of the titration, but the results are not good.)

*Analysis of Metallic Zinc.*

Spelter usually contains small percentages of lead, together with iron, cadmium, arsenic, copper, etc. Classen gives a convenient method for analysis, as follows:—

Carefully weigh from 50 to 100 grams of the zinc, in one piece, and hang by means of a platinum wire in a beaker which is three-fourths full of dilute  $H_2SO_4$ , so that the zinc is about one-half immersed. Only the zinc will be dissolved, as no other metal will go into solution while undissolved zinc yet remains. When a sufficient portion of the zinc is dissolved, filter the solution quickly through a ribbed filter, washing the spongy deposit from the zinc on the filter, as well as the residue. Dry the remaining zinc and weigh; thus obtaining the weight of the zinc operated upon, by difference. Digest the material on the filter with  $HNO_3$ , evaporate to dryness, cool, take up with  $HNO_3$  and water. The residue may contain oxides of tin and antimony, carbon and silica, from which determine the tin and antimony according to previous directions. Determine carbon (by combustion) in a separate sample, as well as silica. Arsenic and antimony are partially lost as hydrides during the solution of the zinc; consequently these metals must be determined in a separate sample. Treat the filtrate from the silica with  $H_2S$ , digest the precipitate with  $K_2S$ , filter, dissolve the residue in  $HNO_3$ , add  $H_2SO_4$  and drive off  $HNO_3$  by evaporation. Take up with water, remove lead sulphate by filtration, precipitate cadmium with  $NH_4OH$  and  $(NH_4)_2CO_3$ , acidify the filtrate and precipitate copper with  $H_2S$ . Make the filtrate from the copper alkaline with ammonia and further examine the precipitate, if any occurs.

### Analysis of Commercial Zinc Ores.\*

(The writer states that lead, iron and lime are usually penalized in the purchase of zinc ores. Sulphur is penalized in calamine by ore-buyers in Missouri; its equivalent in zinc being deducted from the total zinc in the ore. In blende ores it neither entails a penalty nor commands a premium, but an accurate determination of the sulphur in blende ores is required by users of zinc blende for acid making. Cadmium, in excess of 0.12 per cent, is objectionable for making certain brands of spelter, and for oxide manufacture. All of these elements can be accurately and quickly estimated, but unfortunately some of the published methods are very faulty. None of the methods for cadmium given in Furman's generally excellent Manual are based on correct principles; those given in the new edition of Fresenius are more suited for research work, with exception of the Fahlberg method for zinc, which, as described, is unsuited for any purpose. The following analytical methods have been found to give accurate results:)

*Determination of Lead.*—From 0.500 to 3 grams of the prepared sample is decomposed in a casserole with nitric acid (if much calcium carbonate is present in the ore, it must be previously dissolved in very dilute nitric acid; any lead existing in this solution being precipitated by hydrogen sulphide and added to the lime-free residue), evaporated with addition of 2 or 3 cc. of sulphuric acid until white fumes appear, cooled, diluted and boiled to complete solution of all soluble sulphates, filtered and washed with water containing 2 or 3 cc. of sulphuric acid per litre. Distilled water, free from chlorides and ammonia, must be used throughout. The insoluble residue, containing lead as sulphate, is digested with 15 or 20 cc. of hot ammonium carbonate, if its appearance indicates the presence of more than 0.040 or 0.050 grams of lead; it is then filtered, washed, the carbonate of lead dissolved with 5 or 6 cc. of glacial acetic acid (or 15 to 20 cc. of 30% acid), with the aid of heat, and the filtrate

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\*W. Geo. Waring, E. & M. Jour., Vol. 78, p. 298.

therefrom titrated with standard potassium ferro-cyanide (25 grams of pure salt in 2400 cc. of distilled water), using uranium acetate or nitrate indicator and a standard zinc acetate solution for residuary titration. The latter is made by dissolving 7.47 grams of pure, freshly-ignited zinc oxide in a sufficient amount of acetic acid and diluting to 2400 cc. One cc. of either solution corresponds to 0.01 grams of metallic lead. The ferro-cyanide solution alters slowly with time, and must be standardized against pure lead sulphate, or carbonate free from basic lead carbonate, every two or three weeks. The most precise results are obtained when the lead solution is sufficiently diluted and with the use of residuary titration. The solution should not contain more than 0.200 grams of lead in 100 cc. at most. Small amounts of lead (0.050 grams and under) can be most accurately determined gravimetrically, by dissolving the sulphate by repeated boiling with small portions of ammonium acetate, finally washing the insoluble residue on the filter with hot, dilute hydrochloric acid (using 15 to 25 cc. of 25% acid), collecting the filtrate in a clean casserole containing a pellet of *pure* zinc, heating, adding a little more acid if results are wanted quickly, otherwise allowing to stand for an hour or two, or over night. When all of the lead is precipitated, as shown by the filmy appearance of the outer fringes of the sponge, or by testing a portion of the filtrate, after neutralizing, with chromate solution, the spongy lead is separated from the zinc by means of a pointed forceps or splints, washed well with hot water, finally with alcohol, then vigorously compressed into a thin, lustrous disc in the agate mortar, dried between filter-papers and then over sulphuric acid in a desiccator, and weighed. (Compare Method 3 for Lead, under Analysis of Smelting Ores.)

*Determination of Iron.*—This element is usually determined from the ferric hydrate separated in the ordinary zinc assay. The hydrate is reduced by means of sulphuric acid and zinc, or by means of stannous chloride according to the Zimmermann-Reinhardt method. (See Analysis of Iron Ores.) When pure zinc is used as the reducing agent, it is best to have the zinc in large excess since, if kept under water, it may be used repeatedly, with fresh additions from time to time. Only enough sulphuric acid should be used to insure complete reduction,—say 1 cc. of dilute (20% by volume) acid for each 0.005 grams of iron supposed to be present. The acid solution is reduced by filtering through an 8 or 10-inch column of finely-granulated zinc (Jones' reductor) or in a beaker with mossy or coarse granulated zinc; in the latter case it should be heated to boiling for 10 to 15 minutes. When cooled, if a drop of the liquid gives no reaction with acidulated sulpho-cyanate, it is simply washed into a clean beaker, by decantation, acidified with a little sulphuric acid and titrated with standard permanganate.

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*Determination of Lime.*—Treat one gram of the sample with 10 cc. or more of strong hydrochloric acid. When evaporated to one-half, filter and wash; add to the warm filtrate 1 or 2 cc. of nitric acid to oxidize iron. Add 6 or 8 grams of ammonium chloride and 10 to 12 cc. of strong ammonia, boil, filter, and wash with distilled water containing ammonia and ammonium chloride. Re-dissolve the precipitated hydroxides in hydrochloric acid, reprecipitate with ammonia, filter and wash as before. Heat the combined filtrates to boiling, add hot ammonium oxalate solution containing not less than 0.800 grams of the dry salt,—more, if

the sample is rich in lime. Manganese, if present, must be separated with the iron by means of bromine water, ammonium per-carbonate or other per-oxidizing agents (except per-sulphates) before the addition of the oxalate. No lead or zinc will precipitate with the lime in presence of the excess of ammonia and ammonium chloride prescribed, unless a large amount of lead is present. In such case, it is best to re-dissolve and re-precipitate the oxalate. The calcium oxalate, after settling clear (the solution meanwhile having been kept quite hot, but not boiling), is filtered through a Munktell No. 2, or other fine filter, washed first with ammoniated water to prevent clogging of the filter with zinc hydroxide etc., then with pure water; the washed precipitate then being treated in the usual manner for the volumetric determination of the lime by means of permanganate. It is essential to deduct from the final result that of a blank test upon the water and reagents used: The purest materials obtainable will usually show lime equivalent to about 0.03 per cent., even though no turbidity be detected. Ores known to contain but a small amount of lime may be first decomposed with nitric acid. In the case of ores containing lime garnets, or other insoluble silicates of aluminates, the insoluble residue from the acid treatment must, of course, be rendered soluble by fusion or sintering with sodium.

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*Determination of Sulphur.*

(The following method is far superior to any other which has been made known up to the present, both as to accuracy and quickness. When pure manganese dioxide, free from sulphur, shall have been placed within the reach of the analyst, this method will doubtless supersede all others for blende and similar ores.)

Mix and grind together thoroughly in an agate mortar 0.250 grams of the ore, if blende; (or more if an oxidized ore or calcined blende), 0.500 grams of dry sodium carbonate, 0.250 grams of potassium chlorate and, when these have been incorporated, 1.200 grams of pure manganese dioxide. Transfer to a porcelain or platinum crucible, which has been prepared by lining the walls and bottom with a layer of magnesia, pressed into place with the agate pestle. Rinse the mortar with 0.300 grams of additional dioxide, and finally cover the mass with a little magnesia. Heat the crucible over the lamp, at first gently and finally to full redness, maintaining this temperature for 15 or 20 minutes. When cooled, invert the crucible so that the contents will drop into a casserole or beaker containing water. The mass will disintegrate almost immediately if the heat is not too high. Boil with water and proceed exactly as in Eschka's method for coal. (See Analysis of Coal and Coke.) The addition of bromine-water is not necessary. The whole of the sulphur in the ore is now soluble in water, but that contained in the manganese dioxide will, in part, remain insoluble. For exact work it must be determined separately by dissolving the residue in hydrochloric acid, precipitating with barium chloride, re-dissolving the precipitate in strong sulphuric acid and re-precipitating in water. A blank test must be made with each new lot of manganese dioxide.

Sometimes it is necessary that the sulphur in calamines and

calcined zinc ores shall be reported, according to its state of combination. In such case, the sulphur in soluble sulphates is determined in a cold water extract from repeated leachings; in basic and insoluble sulphates (except barium sulphate) by boiling with ammonium carbonate, or with sodium acetate; free sulphur, by extracting with carbon di-sulphide and volatilizing the latter; the total sulphur by the method already described; and barium sulphate by solution of the residue in hydrochloric acid, separation of lead by metallic zinc or hydrosulphuric acid, and precipitation of barium sulphate by very dilute sulphuric acid.

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*Determination of Cadmium and Copper.*

Of the two following methods, the first is the one in general use; the second method is based upon the fact that copper may be separated from cadmium by heating the slightly acid solution with sodium thio-sulphate.

The sample is decomposed with hydrochloric acid or aqua regia, nearly all of the acid is driven off by evaporation, the remainder is diluted, filtered, and to the filtrate sufficient acid is added to bring its acidity up to the equivalent of 10 cc. of hydrochloric acid (sp. gr. 1.10) in 250 cc. of solution. Then treat with hydrogen sulphide, filter off sulphides of copper, cadmium and lead (containing a little zinc and free sulphur), wash with a jet of dilute sulphuric acid into a beaker, boil to dissolve the cadmium and zinc, filter, acidulate the filtrate (or add alkali) in order to make the acidity of the solution about 6.5 per cent., by weight, of sulphuric acid; heat to about 70° and precipitate the cadmium with hydrogen sulphide. The precipitate, containing no free sulphur, is collected on tared filters, washed, dried and

weighed; or, it may be digested with ferric sulphate and titrated with permanganate.

In the second method the ore is decomposed as before and evaporated with sulphuric acid till dense fumes arise; dilute, digest, filter and precipitate copper by heating with sodium thio-sulphate. The solution should be distinctly acid, but any considerable excess of sulphuric acid should be neutralized with soda. Filter off precipitated sulphides and precipitate the cadmium in the filtrate by means of hydrogen sulphide, proceeding as in the first method.

The sulphide residue from either method is available for the determination of the copper, either by ignition, by re-solution in nitric acid, or, when it contains lead, in nitric and sulphuric acid and reprecipitation for gravimetric assay.

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#### Determination of Tellurium and Selenium in Ores.

Whether the ore be apparently thoroughly oxidized or not, it is safer to treat first with strong  $\text{HNO}_3$  in order to oxidize any tellurides and selenides which may be present.

*Operation.*—Treat from one to two assay-tons of the finely pulverized ore (previously dried at  $100^\circ \text{ C}.$ ) in a casserole, with gradual additions of strong  $\text{HNO}_3$ . Cover with a clock-glass and digest at a gentle heat till red fumes no longer appear, cautiously add strong  $\text{HCl}$ , place on the water-bath and evaporate to dryness. Take up with  $\text{HCl}$  with the aid of heat, filter on an asbestos filter with suction, and wash thoroughly. Evaporate the filtrate to about 100 cc., cool, filter again if necessary; to the filtrate add a large excess of solution of  $\text{SnCl}_2$  (Reagent 4) and warm on the water-bath. If tellurium or selenium is present it will separate readily as

a black or brown precipitate. Filter through a Gooch filter (previously weighed), wash with dilute HCl and then with water, dry at 100° C., cool and weigh as residue (a).

This weight represents the tellurium, selenium, and gold. If it is desired to separate the gold at this point, dissolve the tellurium and selenium on the filter by cautious additions of HNO<sub>3</sub>, wash thoroughly and reserve filtrate (a). Melt the asbestos filter and its contents in a crucible, with proper fluxes, and cupel the button for gold.

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*For Selenium and Tellurium.*—Evaporate filtrate (a) to dryness on the water-bath, take up with HCl, precipitate tellurium and selenium with excess of SnCl<sub>2</sub> solution as before, wash, dry and weigh. This residue (or residue (a) above) is then cautiously collected, together with the asbestos filter, and the whole boiled with a strong solution of KCN, in a casserole, for from three to eight hours (generally three hours is ample), the solution being diluted with water as it boils down. Filter through an asbestos filter with suction, wash well with water and reserve residue (b). Place the filtrate on the hot-plate or water-bath, *under the hood*, add an excess of HCl and boil for one hour. Cool, filter through a weighed Gooch filter, wash with water, reserve filtrate (b), dry at 100° C., cool and weigh as metallic selenium.

Treat residue (b) above with strong HNO<sub>3</sub> on the filter, wash and evaporate to dryness on the water-bath. Take up with HCl and add to filtrate (b). To the united filtrates add an excess of SnCl<sub>2</sub> solution as before, heat nearly to boiling, filter through a weighed Gooch filter, wash with dilute HCl, then with water, dry at 100° C., cool and weigh as metallic tellurium.

Results based upon samples weighing assay-ton or fractions thereof, are reported as an "ounce per ton" for each milligram found per assay-ton.

If much arsenic be present, sulphurous acid and not  $\text{SnCl}_2$ , must be used for the first precipitation of the tellurium and selenium. A large quantity of the reagent may be necessary, since all of the arsenic must be reduced before the tellurium and selenium will be precipitated. The complete precipitation is frequently retarded by the presence of too much HCl; this may be remedied by dilution with water.

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*For Lead.*—If lead is present in the ore it may be separated from the original solution after filtering off the gangue.

Dilute this solution with water to which one-eighth of its bulk of alcohol has been added, precipitate the lead with dilute  $\text{H}_2\text{SO}_4$ , evaporate the filtrate from the lead sulphate to about 100 cc. and proceed for the other metals as before.

Silver, if present in the ore, remains as insoluble silver chloride with the silicious residue from the original solution of the ore. It may be collected by washing the residue with solution of  $\text{NH}_4\text{OH}$  and re-precipitation as chloride. The silver chloride is then filtered through a weighed asbestos filter, conveniently using a Gooch crucible, washed, dried at 100° C. and weighed as silver chloride.

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#### Detection and Determination of Cadmium.

The presence of cadmium may be detected by treatment of the acid solution of the substance with  $\text{H}_2\text{S}$  gas, solution of the precipitated sulphides in HCl, removal of bismuth if

present by excess of  $\text{NH}_4\text{OH}$ , acidifying strongly with HCl, removal of copper if present by boiling with addition of  $\text{Na}_2\text{S}_2\text{O}_3$ , neutralizing the filtrate with  $\text{NH}_4\text{OH}$  and precipitating yellow cadmium sulphide with  $(\text{NH}_4)_2\text{S}$ .

*Determination.*—Decompose from 1 to 3 grams of the ore or substance with HCl or, if necessary, with aqua regia. Evaporate to dryness, moisten with 5 to 10 cc. of dilute HCl, take up with hot water, filter and wash with hot water till the bulk is about 100 cc. Treat the filtrate with  $\text{H}_2\text{S}$  gas, filter and wash with water containing  $\text{H}_2\text{S}$ . Dissolve the sulphides in hot HCl with boiling; remove lead, if present, with  $\text{H}_2\text{SO}_4$ , filter and wash. To the filtrate add an excess of  $\text{Na}_2\text{CO}_3$  or  $\text{K}_2\text{CO}_3$  solution, filter, wash thoroughly with hot water and dry. Carefully remove the precipitate from the filter, as far as possible, and place it in a platinum crucible. Carefully ignite the filter separately, after moistening with a strong solution of  $\text{NH}_4\text{NO}_3$ , and add the ash to the precipitate. Ignite carefully to constant weight of  $\text{CdO}$ .

\*There is difficulty in removing all of the  $\text{CO}_2$ , and the result of the above operation is apt to be somewhat too low.

Under Analysis of Zinc Ores two methods are given either of which may be applied to the determination of cadmium in ordinary ores with entire success.

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#### Detection and Determination of Bismuth.

Bismuth may be detected by treating the HCl solution with  $\text{H}_2\text{S}$  gas, solution of the sulphides in  $\text{HNO}_3$ , precipitation as  $\text{Bi}(\text{OH})_3$  with excess of  $\text{NH}_4\text{OH}$ , solution of the hydrate in the smallest adequate quantity of HCl or  $\text{HNO}_3$ , and pre-

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\*Fresenius, 1st Am. Ed., page 324.

cipitation of the basic salt by addition of a large excess of water.

\*Bismuth may also be detected with copper and cadmium by addition to the slightly acid solution of a slight excess of potassium ferri-cyanide. The precipitate is gently heated with an excess of KCN, when the copper and cadmium compounds dissolve, leaving the bismuth as a white flocculent hydroxide. Two portions of the filtrate are separately tested: one for copper by addition of HCl which throws down a brown-red copper ferro-cyanide, the other for cadmium by addition of  $\text{NH}_4\text{OH}$  and  $(\text{NH}_4)_2\text{S}$  which, with gentle heat, yields yellow CdS.

*Determination.*—Dissolve from 1 to 2 grams of the ore or alloy in 10 to 15 cc. of  $\text{HNO}_3$ . (If phosphoric or arsenic acid is present the solution must be made in aqua regia.) If lead is present, evaporate the solution to small bulk and add enough HCl to dissolve all of the bismuth, when the lead all separates as a chloride. Test a portion of the clear liquid with a drop of water; if turbidity is produced, return the portion to the original solution and add more HCl; test again and add more HCl till no permanent turbidity is produced unless several drops of water are added. Add dilute  $\text{H}_2\text{SO}_4$ , stir well and allow to stand some time; add excess of  $\text{C}_2\text{H}_6\text{O}$  (sp. gr. 0.80), stir thoroughly, allow to settle, filter, wash with  $\text{C}_2\text{H}_6\text{O}$  containing a little HCl, then with pure  $\text{C}_2\text{H}_6\text{O}.$ †

The lead may be determined in the residue.

If lead is not present, the  $\text{HNO}_3$  solution is evaporated quite low, 5 cc of HCl are added and a little water. The solution is then nearly neutralized with  $\text{NH}_4\text{OH}$  and a large

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\*Crookes' Select Methods, page 395.

†H. Rose, Pogg. Annalen, 110, 342.

quantity of water is added. Allow to stand for some time and test the clear supernatant liquid for further precipitation by addition of more water.

When the precipitation is complete, filter, wash well with cold water, dry and fuse in a porcelain crucible of adequate size with about six parts by weight of KCN, placing a part of the KCN in the bottom of the crucible, then inserting the filter and bismuth, carefully folded, and finally the remainder of the KCN. The fusion should be conducted at a comparatively gentle heat, and is complete in fifteen minutes. Cool, dissolve in water and separate the grains of metallic bismuth, dry and weigh. Before the fusion weigh the crucible with a small dried filter. After dissolving the fusion, filter, dry and weigh the filter, metallic bismuth and crucible, and subtract the former weight of crucible and filter. This is to avoid contamination of the metallic bismuth in case the crucible is attacked during the fusion.

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#### Analysis of Copper-Nickel-Cobalt Ores, Metal or Products.

(1). *Metal.*—Weigh duplicate samples of 1 gram each, place in an evaporating dish, cover with a watch-glass and digest at a low heat with 15 cc. of water to which 4 or 5 cc. of strong HNO<sub>3</sub> have been added. Evaporate to dryness and take up with 50 cc. of water containing 2 cc. of strong HNO<sub>3</sub>. Pour, filtering if necessary, into a No. 2 beaker and dilute to a 120 or 130 cc. mark. The weight of the platinum cylinder electrode (see Analysis of Copper Ores and Products) being recorded, both electrodes are put in place, and the connecting wires are joined to a battery of two Bunsen cells. Bubbles of oxygen gas should at once rise from

the spiral and the cylinder show a tarnish of deposited copper. Should bubbles arise but no copper be deposited, the solution is too strongly acid and must be partially neutralized with  $\text{NH}_4\text{OH}$ .

If no action whatever takes place, then no current is passing and the connections must be inspected. The action is allowed to go on over night. In the morning detach the electrodes, without previously breaking the current, and wash the cylinder immediately with a small jet of water from the wash bottle, allowing the washings to run into the beaker. The cylinder, after being thoroughly washed in alcohol and the alcohol ignited and burned off, is ready for weighing. The increase in weight shows the amount of deposited copper.

To prepare the cylinder for the nickel electrolysis, dissolve off the copper in strong  $\text{HNO}_3$ , wash first with water, and then with alcohol, burn off the alcohol and weigh. Again attach the electrodes as before and allow the current to pass through the liquid for a minute, in case a deposition of copper appears on the electrode, the current must be continued for two hours longer and the deposited copper treated as before.

The acid solution, now free from copper, is made strongly ammoniacal and the current continued till the solution is colorless. Free ammonia must always be present. The cylinder is washed and dried as before, and weighed to show the amount of deposited nickel. As nickel salts are not so easily decomposed by the electric current as copper salts, it is advisable to add a third Bunsen cell, coupling all three for intensity. Duplicates should not show a difference of more than 5/100 of 1 per cent.

When cobalt and nickel are both present, they will be deposited together on the negative electrode. After finding their combined weight, they may be dissolved in  $\text{HNO}_3$  and separated as hereinafter directed. Either nickel or cobalt being found, the other is determined by difference.

(2). *Ores or Products.*—The quantity to be taken varies with the richness of the substance; the following amounts have been found sufficient:

Per cent. of Copper or Nickel present.	Quantity of substance to be taken.
1 to 5.....	5 grams
5 to 20.....	2 grams
20 to 50.....	1.5 grams
50 to 100.....	1 gram

The weighed quantity of the finely powdered substance is dissolved by evaporating to dryness with 20 to 30 cc. of  $\text{HNO}_3$  to which a few drops of  $\text{H}_2\text{SO}_4$  have been added. Any colored residue left undissolved is generally organic matter or the higher oxides of iron, and may be filtered off. Should much arsenic or antimony be present, 5 cc. of strong  $\text{HNO}_3$  are added to the solution before electrolysis, in order to prevent a deposit of those metals on the copper; otherwise 2 cc. of  $\text{HNO}_3$  are sufficient.

After the electrolysis of the copper has been completed, and the solution made ammoniacal, any precipitation of third group hydroxides should be filtered off before the electrolysis of the nickel is begun.

See also determination of Nickel in Steel and Ferro-Nickel.

*Separation of Nickel and Cobalt.*

*Nickel as NiO.*—The weighed nickel and cobalt, dissolved in HNO<sub>3</sub> and evaporated with a few drops of H<sub>2</sub>SO<sub>4</sub>, are dissolved in water in a platinum or porcelain dish on the water-bath, and KOH added until slight precipitation takes place. Under continuous warming a solution of pure KCN is added until the precipitate which was first formed has entirely re-dissolved, and the solution smells of KCN. After boiling 45 minutes, during which time the solution should not be allowed to decrease in bulk, a paste of freshly prepared HgO and water is added until the precipitate formed is yellow colored. The dish is now allowed to stand in a warm place for an hour, and when cool is then filtered, the precipitate washed and ignited in a weighed crucible *under the hood*, until constant weight is obtained. NiO × 0.7858 = Nickel.

*Cobalt as Co.*—The filtrate is carefully neutralized with HNO<sub>3</sub> and precipitated with a nearly neutral solution of mercurous nitrate; filter and wash the precipitate and, after transferring it to a weighed Rose crucible, ignite with a Bunsen burner and further ignite at a red heat in a stream of hydrogen until the metallic cobalt remains. After weighing, test the residue for an alkaline reaction; if such appears, wash the residue with boiling water, dry and again ignite in the hydrogen stream.

### Cyanide Assay for Gold Ores.

In the cyanide treatment of gold and silver ores, as in all other processes, it is desirable to extract the greatest part of the precious metals at the least expense; or, to obtain a high extraction with the least consumption of cyanide. Many substances occur in ores, and in waters which may be available for making solutions, which destroy cyanide; therefore, if proper laboratory tests do not yield results which would be commercially successful, the process should not be abandoned before complete analysis of the ore, and "acidity" tests be made; and until the waters used be also analyzed and tested for carbonic acid, free sulphuric acid and soluble sulphates. Further: Dr. Scheidel says: "The cyanide solution will in many cases contain, after treatment of ore, the evidence of secondary reactions; and a complete chemical analysis of the solution, before it comes into contact with the zinc, should in all cases be made. The explanation of unsatisfactory results with cyanide treatment will be found, in many instances, by means of such an examination." The following method for the examination of ores, to determine their amenability to cyanide treatment is arranged by Mr. A. J. Morse:—

After the ore is assayed for gold and silver, a careful average sample is crushed to a 30-mesh. This size is used simply because it may be considered as being more nearly an "usual" size in mill-practice, and therefore more convenient under certain forms of crushing, if extraction tests also show it to be satisfactory. Prepare a 1% solution of pure KCN (Reagent 29-a) and a standard solution of AgNO<sub>3</sub> (Reagent 29-b). Prepare two burettes, one containing the KCN solution, the other distilled water. Into eight 4-ounce, glass-stoppered tincture bottles place samples of the ore as prepared above—one assay-ton, carefully weighed, in each bottle. Into bottles numbered 2, 4, 6, and 8 put 0.100 grams of c. p. CaO. Bottles numbered 1, 2, 3, 4 will be tested for 24 hours' time; bottles 5, 6, 7, 8 will be tested for 48 hours. Bottle No. 1 will be tested with a 4-pound (or 0.2%) solution of cyanide; No. 2 with an 8-pound (or 0.4%); No. 3

with a 12-pound (or 0.6%); No. 4 with a 16-pound (or 0.8%) solution. Bottles Nos. 1 and 5 will be tested with a 4-pound (or 0.2%) solution of cyanide; Nos. 2 and 6 with an 8-pound (or 0.4%) solution; Nos. 3 and 7 with a 12-pound (or 0.6%) solution; and Nos. 4 and 8 with a 16-pound (or 0.8%) solution. If it is found to be necessary, other strengths of solution and other times may be tried later.

With each assay-ton of ore, in each bottle, one assay-ton of solution is used, or (roughly) 30 cc. In bottles 1 and 5 a 4-pound, or 0.2%, solution is made as follows:—In 30 cc. of a 0.2% solution there are 0.060 grams of cyanide, corresponding to the amount contained in 6 cc. of the standard or 1% solution. Therefore, in bottles 1 and 5, place 30 cc. of a solution made up of 24 cc. of distilled water and 6 cc. of Reagent 29-a. If this solution were then titrated with Reagent 29-b, 10 cc. of the solution would be found to require 4 cc. of the standard silver nitrate; thus indicating a strength of 4 pounds, or 0.2%, per ton.

Prepare the other groups of bottles in a similar manner; for bottles 2 and 6 using 18 cc. of distilled water and 12 cc. of Reagent 29-a; for bottles 3 and 7 using 12 cc. of distilled water and 18 cc. of Reagent 29-a; and for bottles 4 and 8 using 6 cc. of distilled water and 24 cc. of Reagent 29-a. Measure these solutions into the eight bottles containing the ore, mix by giving a circular motion, cork and let stand. Remove stoppers and stir up solutions three or four times in 24 hours, preserving similar conditions throughout the set.

At the end of 24 hours, take off the first four bottles, filter, and, without washing, take 10 cc. from the clear filtrate from each bottle and titrate with Reagent 29-b. The difference between the original strength of the solution and the

strength found represents the consumption of cyanide in pounds per ton. After titrating, wash the ore thoroughly, dry, place in a crucible with proper fluxes and assay. From this assay of the tailings, calculate the per cent. of extraction by cyanide. At the end of 48 hours, repeat the above operation on the last four bottles.

The bottle or bottles showing the best extraction indicate the time necessary and the strength of cyanide to be employed. If the bottles containing CaO show less consumption of cyanide than those without it, an acid condition of the ore is indicated and CaO is necessary. The necessary amount of CaO may be calculated by shaking 100 grams of the ore with 100 cc. of water containing 10 cc. of a standard solution of NaOH; after shaking for from five to ten minutes, an aliquot part of the solution is drawn off and the excess of alkali is determined by titration with standard H<sub>2</sub>SO<sub>4</sub>.

If an excessive consumption of cyanide occurs in the bottles containing CaO, the presence of copper, zinc or other deleterious substances is indicated, and the ore must be analyzed to determine their character and quantity; experiments must also be made to determine the possibility of the removal of these substances by preliminary washing, by treatment with sulphuric acid, by roasting or other means.

Further bottle tests should then be made, using in each bottle the particular solution (with or without CaO) which is indicated by previous tests to be most efficacious; but in this series of tests, the ore in each pair of bottles should be crushed to a different degree of fineness,—say 16, 20, 26, and 40-mesh.

Should the extraction be unfavorable in the above tests, make an amalgamation test upon from 4 to 6 assay-tons of the ore, in a copper-bottomed, amalgamated gold-pan; save

the tailings and assay the same; concentrate these tailings by use of a horn or a gold-pan, and repeat the concentration several times. Assay the concentrates and the final tailings; then repeat bottle tests on these tailings.

Finally, having determined the best mode of treatment for the ore, the results should be confirmed upon a larger scale, as follows:—

Take three small wooden tubs, bore a hole in the bottom of each, and connect them by means of rubber tubes provided with pinch-cocks; and paint the tubs with "P & B" paint. In one tub mix a cyanide solution of the strength shown to be most favorable; in the next tub (placed below and somewhat in front of the first) place a false bottom of cotton cloth fastened to a wooden grating, and fill the tub with a weighed quantity of the ore, which has been crushed to the proper size and which has been mixed with the proper quantity of CaO. Connect with the tub containing the cyanide solution, and allow that solution to enter the bottom of the tub containing the ore, and to gradually percolate upwards and saturate the ore. Allow to stand during the time shown to be most favorable by test, and allow to flow into a third tub (placed below and somewhat in front of the middle tub) washing the ore with water till the filtrate shows no KCN.

This operation may be varied by allowing the solution to stand on the ore for 12 hours, then drawing it off into bottom tub and replacing it by a fresh solution run *on top* of the ore; this is allowed to remain 12 hours and the operation is continued till the requisite time of leaching has expired, when the ore is washed as before.

Another variation in this operation consists in allowing the first solution to stand 12 hours, then allowing it to filter off; when the top of the ore is just exposed to the air, fresh

solution is allowed to run on the ore, *slowly*, to replace the solution being filtered off; this operation may be repeated, with occasional assaying of both ore and solution, until such time as the extraction may be found satisfactory.

The preliminary bottle-tests should be considered as indicative of the proper process, though not conclusive; since the bulk test cannot be made under exactly the same conditions, but should be made to correspond more nearly to actual mill-practice.

In conducting the above operation, the KCN solution which accumulates in the lowest tub is caused to flow into and through a precipitating-box containing zinc shavings (see any standard work on cyanide practice for construction of this box), and the residual solution, flowing from the zinc box, returned to the highest tub.

At the end of the operation, the contents of the zinc box is placed in a stone jar and dissolved in dilute  $H_2SO_4$ ; the insoluble residue remaining is filtered, washed, dried, scorified and cupelled. The resulting button is assayed for gold and silver, and the result should correspond very closely with that found by calculation made from assay of the tailings and solution.

*Assay of Cyanide Solutions.*—In a large beaker place any desired volume of solution, up to 20 assay-tons (600 cc.) or more, according to the supposed richness of the solution and the accuracy desired in the assay. Make quite strongly acid with HCl and bring to a boil; while boiling pass  $H_2S$  gas into the solution, maintaining the boiling and passing a strong current of gas for from 15 to 20 minutes. If the precipitate is very slight, add a little solution of lead acetate while passing the gas. Filter by means of a filter-pump. Dry the precipitate and paper, burn off the latter in a scori-

fier or in a 5-gram crucible, scorify with lead, or add fluxes and run crucible assay; cupel, weigh bead, and divide result by the number of assay-tons of solution taken.

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The following method for the cyanide assay appeared in the former (3d) edition of this book. It has been submitted for revision to Mr. C. W. Merrill, who has kindly made some changes, and has supplied the method for Solution Assay, which he says "is the only one, of over a dozen put forward and tested, which can successfully compete with evaporation, fluxing and crucible melting," in the treatment of Homestake ores.

*Operation.*—Prepare a standard solution of potassium cyanide (Reagent 29-c), also a standard solution of silver nitrate (Reagent 29-d). Make a fire assay of the ore to be tested. Determine the acidity in one assay-ton of the 30-mesh sample, by agitating with water for twenty minutes and subsequent titration of this solution with n/10 NaOH. Treat the washed residue with a measured amount of n/10 NaOH; agitate briskly for one-half hour, and titrate the filtrate with deci-normal acid, to determine the alkali used. The total acidity found by the two tests is due: (1) to soluble salts, usually sulphates, and (2) to basic salts.

Place from one to three assay-tons of the sample (according to the richness of the ore), in each of eight soda bottles, which are provided with rubber clamp stoppers. Correct the acidity, if necessary, in each portion, by addition of the necessary weight of lime (which is preferable to soda). Place in the bottles 60 cc. of 0.1%, 0.2%, 0.3% and 0.4% cyanide solution for each ton of ore (these strengths of cyanide are prepared by diluting the standard cyanide solution), thus obtaining two portions of ore treated with 0.1% cyanide, two portions treated with 0.2% cyanide, and

so on. Label each bottle as it is filled. Attach the eight bottles to a shaft which is revolved at the rate of about eighteen revolutions per minute; the temperature being about 60° F. After eighteen hours, remove four bottles, leaving duplicates to be further agitated.

Treat the contents of the four bottles which have been removed as follows:—Filter each, washing each sample of ore onto its own filter *with its own filtrate*. The filtrates must *not* be diluted until they are tested for loss of cyanide. Take 10 or 20 cc. of each filtrate, and determine the loss of cyanide by titration with standard silver nitrate solution (Reagent 29-c). After this determination has been made in each sample, wash them carefully with water; adding the washings to the proper filtrates. The samples are then dried and assayed by the ordinary fire assay, and the results checked by the assay of the solutions.

If the extraction is not satisfactory, the remaining four samples, which have been agitated 36 hours, are treated in a similar manner.

If the extraction is not yet satisfactory, the operation should be repeated upon the same number of samples, each of which, after weighing, should be roasted.

If the agitation tests show that the cyanide process is suited to the ore, tests should then be made by percolation, since the latter method is less expensive. The leaching of the ore by cyanide may be conveniently performed in a large glass percolator, the neck being closed by means of a rubber tube and clip. The filter bed may be made of pebbles covered with a piece of flannel or filter paper, or simply twilled cloth.

Several samples, similarly prepared as before, are placed in their respective funnels and allowed to digest with solu-

tions of cyanide approximating in strength to that which was found most desirable by the agitation method, but for longer times than were found necessary before. The results are calculated as before.

\**Solution Assay.*—To a measured quantity of the cyanide solution, in a beaker, add 10 to 15 cc. of a 10% solution of lead acetate and 3 to 4 grams of zinc dust. Make acid with about 20 cc. of HCl, and boil until action ceases. The lead will be found in a spongy mass; filter, wash on the filter twice, remove paper and residue from the funnel, and dry between blotters. Place in a scorifier, cover with about 15 grams of test-lead and some borax glass; add a small piece of silver foil, and melt. Cupel the resulting button, and part for silver and gold.†

#### *Colorimetric Solution Assay.*

In practice, a quick method for the assay of low-grade sump-solutions is of considerable value, even if the method be only approximate. The following method avoids the necessity of melting and cupellation, weighing and parting the bead; generally speaking, it may be considered as only giving approximate results; but, with practice, something better than this may be attained.

From two to ten assay-tons of the low-grade solution are taken for assay, according to the probable gold content; a sufficient quantity of stronger cyanide solution is added to induce active precipitation, and the sample is boiled with addition of zinc dust or shavings, then filtered on a small filter.

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\*Method arranged by Mr. Allan J. Clark, Assayer, Homestake Mining Co.

†This lead may, more conveniently, be collected, the moisture pressed out with a spatula, and the residue cupelled without scorification. In the use of this modification, however, more lead is reduced, that a larger button may be formed; and some practice with the method may be necessary.

The residue is treated, in a small beaker, with  $\text{HNO}_3$  until residual zinc is dissolved, a small amount of  $\text{HCl}$  is added to dissolve the gold, and the whole is evaporated till only a small solution remains, which is diluted and taken up with a small amount of water. An aliquot part of this solution is treated with a few cc. of a solution of stannous chloride, and shaken up in a Nessler tube. In an exactly similar tube, a volume of a standard solution of gold chloride, containing an amount of gold approximate to that in the other tube, is placed and treated with the same volume of stannous chloride, and also shaken up. The two tubes are compared, the stronger solution is diluted with water till the purple colors agree, and the gold is calculated.

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#### Chlorination Assay for Gold Ores.

(a) *To Determine Adaptability to Barrel-Chlorination.*—The ore should be crushed to 30-mesh, as that size closely approximates actual mill-practice.

Sample carefully and make a fire assay.

If the ore contains a visible amount of sulphurets, the sample taken for chlorination should be roasted; if not, three samples may be treated raw and three roasted, as follows:

Weigh out six portions of one assay-ton each, place them in six securely stoppered, four-ounce bottles, and label A, B, C, D, E, and F, after carefully roasting A, B, and C. Weigh of bleaching powder two portions of 0.291 grams, and label A and D; two of 0.437 grams and label B and E; and two of 0.583 grams and label C and F. Make these weights in six weighing flasks, and put in the stoppers till

used. Make similar weights of  $H_2SO_4$  (60° B.) and place in six similarly labelled flasks. Moisten all of the ore-samples with water and, to samples A and D add about two-thirds of the bleaching powder in bottles A and D, and about two-thirds of the  $H_2SO_4$  in bottles A and D, and cork tightly. Treat the other ore-samples similarly, with their respective portions of bleaching powder and  $H_2SO_4$ .

Attach all of the bottles to a revolving shaft, or place in a shaker, and agitate for four hours; add the remaining bleaching powder and  $H_2SO_4$ , each part to its proper bottle and agitate four hours longer. On opening the bottles there should be free chlorine present, as indicated by its fumes with  $NH_4OH$ . Fill each bottle two-thirds full of water, shake and decant on a filter. Afterward rinse each portion on its proper filter and wash with hot water till the washings give no test for chlorine. Dry each sample of pulp, place in a crucible with proper fluxes and assay. The loss of gold equals the amount extracted. Calculate the percentage of extraction.

In the treatment of the three pairs of samples, we have added amounts of bleaching powder and  $H_2SO_4$  corresponding respectively to 20, 30, and 40 lbs. of these reagents per ton of ore. Should the extraction in any case be satisfactory, further tests may be similarly made under *neighboring* conditions as to time and amount of chlorine, to determine the most favorable condition. Should none of the above tests yield a satisfactory extraction, a second series of tests should be made, increasing the amount of bleaching powder and  $H_2SO_4$  to an amount corresponding, with the three pairs respectively, to 50, 60, and 70 lbs. per ton of ore.

(b) *Determination of Gold in the Wet Way.*—If the substance is an ore, a finely pulverized and dried portion, of one or two assay-tons or fraction thereof (according to the richness of the ore) is treated with strong  $\text{HNO}_3$  and allowed to digest on the water-bath till red fumes no longer appear,\* excess of  $\text{HCl}$  is added and the mass evaporated to dryness, preferably on the water-bath. The substance is taken up in  $\text{HCl}$ , diluted with water and filtered.

From this solution the gold is usually precipitated by excess of either hydro-sulphuric acid, stannous chloride or ferrous sulphate; or, if the filtrate from the gold is to be further examined, and it is not desirable to introduce any foreign metals, the precipitation of the gold may be made by oxalic acid.

(1) *By Hydro-Sulphuric Acid.*†—Sulphides are precipitated in the above solution as usual, the precipitate is washed and heated with  $\text{HCl}$  (sp. gr. 1.11) which dissolves the sulphides of antimony, tin, cadmium, bismuth and lead. The residue is carefully washed and then treated with  $\text{HNO}_3$  to remove sulphides of copper and arsenic.‡ After filtration, the residue contains the gold with sulphides of platinum and mercury, if present. The mercury is removed by ignition and the platinum as below.

(2) *By Stannous Chloride.*—By the use of this reagent metallic gold is quickly precipitated on warming, together with mercury, arsenic, tellurium and selenium, if present. The residue, treated with  $\text{HNO}_3$  and washed, gives metallic gold on ignition.

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\*To oxidize and prevent loss of the sulphur metals.

†Antony and Niccolli., Gaz. ch. ital., 22, 11, 408.

‡Also removing tellurium and selenium.

(3) *By Ferrous Sulphate.*—Metallic gold is precipitated. The solution should stand for from 12 to 24 hours before filtration.

(4) *By Oxalic Acid.*—The above solution of the ore should be evaporated almost to dryness to remove all of the HCl. The residue should be taken up in a small quantity of very dilute  $H_2SO_4$  and diluted with water. The addition of an excess of oxalic acid, preferably with a small amount of ammonium oxalate, serves to precipitate metallic gold, free from platinum if present. The solution should be allowed to stand in a warm place for from 12 to 24 hours.

If the substance under examination is an alloy, the solution is made in  $HNO_3$ , in which case gold, platinum and oxides of antimony and tin are left undissolved and the gold is separated as below.

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*Separation of Gold from Platinum.*—The ignited residue of gold and platinum is cupelled with three parts by weight of metallic silver and a little lead. The bead obtained is rolled or hammered very thin and treated with  $HNO_3$  which dissolves the platinum and silver, leaving the gold undissolved.

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*Separation of Gold from Iridium.*—Iridium is insoluble in aqua regia.

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*Separation of Gold from Palladium and Rhodium.*—The metals are cupelled with three parts of silver, and parted

with  $\text{HNO}_3$  as usual, in which process the palladium is dissolved. The gold and rhodium are fused in a platinum crucible with bi-sulphate of potassium, the liquid is poured off before cooling and more of the salt added and fused. This operation is continued until the slag is only slightly colored, indicating that the rhodium has all been slagged off as a double sulphate of rhodium and potassium. The fusion is then dissolved in distilled water and the gold recovered, ignited and weighed.

# APPENDIX.

## INTERNATIONAL ATOMIC WEIGHTS, 1903.

		O = 16	H = 1.			O = 16	H = 1.
Aluminium.	Al	27.1	26.9	Molybdenum...	Mo	96.0	95.3
Antimony ..	Sb	120.2	119.3	Neodymium...	Nd	143.6	142.5
Argon .. .	A	39.9	39.6	Neon .. .	Ne	20.0	19.9
Arsenic.....	As	75.0	74.4	Nickel.....	Ni	58.7	58.3
Barium.....	Ba	137.4	136.4	Nitrogen.....	N	14.04	13.93
Bismuth.....	Bi	208.5	206.9	Osmium.....	Os	191.0	189.6
Boron.....	B	11.0	10.9	Oxygen.....	O	16.00	15.88
Bromine.....	Br	79.96	79.36	Palladium.....	Pd	106.5	105.7
Cadmum.....	Cd	112.4	111.6	Phosphorus.....	P	31.0	30.77
Cæsium.....	Cs	133.0	132.0	Platinum.....	Pt	194.8	193.8
Calcium.....	Ca	40.1	39.8	Potassium.....	K	39.15	38.86
Carbon.....	C	12.00	11.91	Praseodymium	Pr	140.5	139.4
Cerium.....	Ce	140.0	139.0	Radium.....	Ra	225.0	223.3
Chlorine.....	Cl	35.45	35.18	Rhodium .. .	Rh	108.0	102.2
Chromium.....	Cr	52.1	51.7	Rubidium .. .	Rb	85.4	84.8
Cobalt.... .	Co	59.0	58.56	Ruthenium .. .	Ru	101.7	100.9
Columbium (Niobium)	Cb	94.0	93.3	Samarium .. .	Sm	150.0	148.8
Copper.....	Cu	63.6	63.1	Scandium .. .	Sc	44.1	43.8
Erbium .. .	E	166.0	164.8	Selenium .. .	Se	79.2	78.6
Fluorine.....	F	19.0	18.9	Silicon .. .	Si	28.4	28.2
Gadolinium	Gd	156.0	155.0	Silver .. .	Ag	107.93	107.12
Gallium.....	Ga	70.0	69.5	Sodium .. .	Na	23.05	22.88
Germanium.. .	Ge	72.5	71.9	Strontium .. .	Sr	87.6	86.94
Glucinum (Beryllium).	Gl	9.1	9.08	Sulphur .. .	S	32.06	31.83
Gold.....	Au	197.2	195.7	Tantalum .. .	Ta	188.0	181.8
Helium.....	He	4.0	4.0	Tellurium .. .	Te	127.6	126.6
Hydrogen.....	H	1.008	1.000	Terbium .. .	Tb	160.0	158.8
Indium.....	In	114.0	113.1	Thallium .. .	Tl	204.1	202.6
Iodine.....	I	126.85	125.90	Thorium .. .	Th	232.5	230.8
Iridium.....	Ir	193.0	191.5	Thulium .. .	Tm	171.0	169.7
Iron.....	Fe	55.9	55.5	Tin .. .	Tn	119.0	118.1
Krypton.....	Kr	81.8	81.2	Titanium .. .	Ti	48.1	47.7
Lanthanum .. .	La	138.9	137.9	Tungsten .. .	W	184.0	182.6
Lead.....	Pb	206.9	205.35	Uranium .. .	U	238.5	236.7
Lithium.....	Li	7.03	6.98	Vanadium .. .	V	51.2	50.8
Magnesium .. .	Mg	24.36	24.18	Xenon .. .	X	128.0	127.0
Manganese .. .	Mn	55.0	54.8	Ytterbium .. .	Yb	178.0	171.7
Mercury.....	Hg	200.0	198.5	Yttrium .. .	Yt	89.0	88.3
				Zinc .. .	Zn	65.4	64.9
				Zirconium .. .	Zr	90.6	89.9

The Atomic Weights used in this book are taken from the first column of figures in the above list, the basis for which is Oxygen = 16.

Those using the above table should be careful that they do not confound the two systems.

**RULES FOR WEIGHING.**

1. Level and adjust the balance.
  2. Always place the substance to be weighed upon the same pan of the scale—most conveniently upon the left.
  3. Never place the substance upon the naked pan; use counterpoised watch-glasses, or a weighed porcelain or platinum dish. Never use paper.
  4. Always bring the balance to a rest before placing upon the pans or removing therefrom a substance or weight.
  5. Use forceps, if possible, in placing upon and removing dishes from the pan.
  6. Always handle weights with forceps; never touch them with the hand.
  7. Never weigh a vessel or substance while warm.
  8. Never try weights at random; commence with the weight nearest to, and less than the substance, and add the weight next in succession till the correct weight be obtained.
  9. Liquids and solids which are volatile, or give off or absorb moisture when exposed to the air, must be weighed in closed vessels. All other substances may be weighed in the open air.
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**ON THE USE OF PLATINUM VESSELS.**

The following substances should not be fused in platinum vessels:

- (1) The caustic alkalies, including baryta and strontia, their cyanides and hydrates.
- (2) Fusible metallic sulphides, or mixtures of sulphides with carbon; especially the alkaline sulphides.

(3) Phosphates and carbon, which at a high heat form platinum phosphide.

(4) Metals that are easily fused, or metallic oxides that are easily reduced. These form fusible alloys with platinum.

(5) Chlorine and all mixtures that liberate chlorine either in the cold or by heat; such as fusible mixtures of a metallic chloride and a nitrate, or of ammonium sulphate and a chloride.

Platinum crucibles may be cleaned by fusing borax or potassium bi-sulphate in them, and dissolving the fused mass in boiling water. Sometimes they may be cleaned by fusing ammonium chloride in them, or by digesting with dilute HCl. To brighten them, scour with sea-sand and water; do not use sharp sand or emery.

### Crucibles.

Silver crucibles, preferably those which are gold lined, should be used for fusions with caustic soda or caustic potash. Use an alcohol lamp or a flame containing no sulphur.

Rose crucibles are used for ignitions in certain peculiar atmospheres, such as oxygen or hydrogen. They are made of porcelain, with a perforated cover connected with a perforated tube.

## REAGENTS.

*(Referred to in the text by numbers.)*

### 1. Fusing Mixture.

Pulverize very finely and thoroughly mix 2 parts  $\text{NaHCO}_3$ , 2 parts  $\text{K}_2\text{CO}_3$ , and one part  $\text{KNO}_3$ . Or, 2 parts  $\text{Na}_2\text{CO}_3$  and one part  $\text{KNO}_3$ . These salts should be chemically pure, and free from sulphur. If the latter is present in the mixture, its amount must be determined by analysis.

### 2. Fused $\text{KHSO}_4$ .

Heat some of the salt in a platinum dish or crucible to quiet fusion, pour it on a porcelain slab. When cold pulverize and place in a salt mouth bottle.

### 3. Magnesia Mixture.

No. (1).	No. (2).
$\text{MgCl}$ ..... 101.5 grams.	$\text{MgSO}_4$ ..... 100 grams.
$\text{NH}_4\text{Cl}$ ..... 200 grams.	$\text{NH}_4\text{Cl}$ ..... 200 grams.
$\text{NH}_4\text{OH}$ ..... 400 cc.	$\text{NH}_4\text{OH}$ ..... 400 cc.
Water to make one litre.	Water ..... 800 cc.
I cc. = { 0.0355 grams $\text{P}_2\text{O}_5$ .	I cc. = about 0.01 grams of P.
	, 0.0154 grams P.

### 4. Stannous Chloride.

Dissolve 50 grams of the crystallized salt in half strength  $\text{HCl}$ .

### 5. Mercuric Chloride.

A saturated solution in water; 60 grams per litre.

### 6. Molybdate Solution.

(a) Take 3 grams of ammonium molybdate, add 2 cc. of  $\text{NH}_4\text{OH}$  and triturate in a mortar; then add 20 cc. of water, which should cause solution; now pour this solution slowly into 20 cc. of  $\text{HNO}_3$  (1.20 sp. gr.), keeping it cold.

(b) Dissolve 100 grams of  $\text{MoO}_3$  in a mixture of 300 cc. of strong  $\text{NH}_4\text{OH}$  and 100 cc. of water. Take 1250 cc. of  $\text{HNO}_3$  (1.20 sp. gr.). Pour a little of this solution into the one above, then pour all of the above solution into the  $\text{HNO}_3$ , rapidly.

These solutions should stand several days before use.

(c) *Wood's Formula*.—One pound of  $\text{MoO}_3$  is mixed with 1200 cc. of water in a stone jar; 700 cc. of  $\text{NH}_4\text{OH}$  (0.88 sp. gr.) are stirred in till the solution is complete, and 300 cc. strong  $\text{HNO}_3$  are added. In each of four 2½-litre bottles is placed a mixture of 500 cc. of  $\text{HNO}_3$  (sp. gr. 1.42) and 1200 cc. of water. Pour into each bottle 550 cc. of the molybdate solution, rotating the bottle and letting the solution flow in quickly. Filter before using.

### 7. Solutions for Volumetric Phosphorus—Handy's Method.

(a) *Pure Yellow Precipitate for standardizing NaOH Solution* (b).—Precipitate from acidified solution of ammonium or sodium phosphate. Wash with 1 per cent.  $\text{HNO}_3$ , dry at 100° C. and keep in glass-stoppered bottles.

(b) *Standard NaOH Solution*.—Dissolve 15.4 grams of  $\text{NaOH}$  in 100 cc. of water, add saturated solution of  $\text{Ba}(\text{OH})_2$  till the precipitation is complete. Filter at once and dilute to two litres.

(c) *Standard HNO<sub>3</sub> Solution*.—Make up 200 cc. of

$\text{HNO}_3$  (sp. gr. 1.42) to two litres, with water, for a *stock* solution. Dilute 200 cc. of this solution to two litres, for a *standard* solution, and titrate against (b) above. Next, treat 0.100 grams of (a) with (b) and test with (c), finally making 1 cc. equal 0.0002 grams of phosphorus, or 0.01 per cent., when two grams are taken of the sample analyzed.

(d) *Phenol-phthalein Indicator*.—Dissolve about one-half gram in 200 cc. of 95% alcohol.

#### 8. Acid Solution of Ammonium Nitrate.

Water .....	1 litre
$\text{NH}_4\text{NO}_3$ .....	100 grams
$\text{HNO}_3$ (sp. gr. 1.40).....	15 cc.

#### 9. Purified Nitric Acid (1.40 sp. gr.)

It must be free from nitrous acid. If the bottle containing the acid shows red fumes, blow air through the acid until the red fumes disappear, then add 5 per cent. of water and set in a dark place.

#### 10. Nitric Acid (1.20 sp. gr.)

Add an equal volume of water to the strong (1.40 sp. gr.) acid. It must be free from  $\text{HCl}$  and chlorine.

#### 11. Hydrochloric Acid.

It must be free from chlorine. If chlorine is present add strips of copper, let stand until it will not give a test for chlorine and distill.

**12. Reagents for Nickel in Anodes.**

1. 50 grams  $K_2C_2O_4$  in 500 cc. of water.
2.  $2\frac{1}{2}$  grams KI in 100 cc. of water.
3. 1.33 grams  $AgNO_3$  in 1000 cc. of water.

**13. Tartaric Acid.**

Tartaric Acid.....	40 grams
Water .....	200 cc.
$BaCl_2$ solution.....	10 cc.

Boil the solution, then allow it to stand till the precipitate has completely subsided and filter off the clear liquid for use.

**14. Purified Asbestos.**

Place a quantity of good, fibrous asbestos in a beaker, add some  $Cr_2O_3$  solution, then enough strong  $H_2SO_4$  to thoroughly saturate, and heat for some time; pour the mass into a funnel and wash, first with water acidulated with  $H_2SO_4$  then with pure water, until the  $Cr_2O_3$  and  $H_2SO_4$  are removed, then dry.

**15. Silicon Mixture.**

One part of  $H_2SO_4$  (sp. gr. 1.84), two parts of  $HNO_3$  (sp. gr. 1.20). (111)

**16. Oxide of Zinc Paste.**

Fill a large sand or clay crucible with commercial zinc oxide, cover and heat in a furnace at a bright red heat for some time, cool and triturate with water to form a thin paste. If the  $ZnO$  contains manganese (as is frequently the

case) it must be dissolved in HCl by addition of excess of ZnO, the manganese precipitated by addition of bromine, the solution filtered, and the ZnO re-precipitated by NH<sub>4</sub>OH, carefully avoiding an excess. Filter, wash and dry. It should not reduce KMnO<sub>4</sub>.

### 17. Solution of Zinc Sulphate.

Dissolve 50 grams of ZnSO<sub>4</sub> in water and dilute to 100 cc.; to this add KMnO<sub>4</sub> solution until a faint pink color is produced; then add some oxide of zinc paste and shake thoroughly; allow it to subside, then filter off the clear solution for use.

### 18. Dry, granular CaCl<sub>2</sub> free from CaO.

Take crystallized calcium chloride in a porcelain dish and heat very carefully (not above 200° C.), till fused, then stir constantly till granulated; transfer the dish to an air-bath and heat at 200° C. till perfectly dry. Keep in well stoppered bottles. After filling the U-tubes, pass dry CO<sub>2</sub> through them for one hour, then dry air till the CO<sub>2</sub> is removed.

### 19. Solution of MnSO<sub>4</sub>, for Iron.

One pound of MnSO<sub>4</sub> and 400 cc. of H<sub>2</sub>SO<sub>4</sub>. Dilute to 2½ litres.

### 20. Zimmermann-Reinhardt Reagents for Iron.

(a) One pound of SnCl<sub>2</sub> is dissolved in one pound of HCl (sp. gr. 1.20), to which water has been added; when solution is complete, dilute to 1 litre.

- (b) A solution of HCl of sp. gr. 1.10.
- (c) A saturated solution of  $HgCl_2$  in hot water; filtered when cold.
- (d) Dissolve 160 grams of  $MnSO_4$  in water, and dilute to 1750 cc. Add to this 330 cc. of phosphoric acid (1.70 sp. gr.) and 320 cc. of  $H_2SO_4$  (sp. gr. 1.84).
- (e) Dissolve 6.79 grams of pure  $KMnO_4$  in 4 litres of water; let stand four or five days, decant, and filter the last 300 cc. through asbestos. The solution should be occasionally standardized against fresh solutions of pure iron. As prepared above, one-half the number of cc. consumed in titrating the iron in a sample of ore weighing 0.600 grams equals the per cent. of iron.

### 21. Solution of $ZnSO_4$ , for Sulphur in Iron.

Dissolve 150 grams  $ZnSO_4$  in 400 to 500 cc. of water, add 400 cc. of strong  $NH_4OH$  and about 7.5 grams of starch in solution, then make up to  $2\frac{1}{2}$  litres with water.

### 22. Starch Indicator.

Take one part of starch, triturate in a mortar with cold water, pour over it 200 parts of boiling water and boil a short time. Allow it to cool and settle, draw off the clear liquid for use.

### 23. Standard Iodine, for Sulphur in Iron. .

Dissolve 4 grams of iodine in 75 cc. of water containing 10 grams of KI; after solution, dilute to 1000 cc. with water. Determine its value by titrating with standard  $Na_2S_2O_3$ , or, preferably, by comparing with a steel standard, making its

strength, for 1 cc., equal 0.01 per cent. sulphur when 5 grams of sample are taken.

#### 24. Reagents for Carbon Determination.

(a) *Double Chloride of Copper and Potassium.*—

$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ .....	170.1 grams
KCl .....	149.2 grams
Water .....	1000 cc.

The solution should be filtered through ignited asbestos.

(b) *Chromic Acid Solution.*—

Dissolve 30 grams of chromic acid in the least quantity of water; add 300 cc. of pure, strong sulphuric acid and heat nearly to boiling.

#### 25. Ammonium Sulpho-Carbonate.

Add one part by volume of carbon di-sulphide to 10 parts of  $\text{NH}_4\text{OH}$ , shake well and allow to stand for several days. To this solution add four times its volume of water. The resulting compound contains ammonium sulpho-carbonate and sulpho-cyanide, according to the following equation:—

$$4\text{NH}_4\text{OH} + 2\text{CS}_2 = 4\text{H}_2\text{O} + (\text{NH}_4)_2\text{S}, \text{CS}_2 + \text{NH}_4\text{CNS}.$$

#### 26. Cadmium Chloride Solution.

Dissolve 250 grams of  $\text{CdCl}_2$  in water, add sufficient  $\text{NH}_4\text{OH}$  to dissolve any residue, heat, filter if necessary, and dilute to four litres with strong  $\text{NH}_4\text{OH}$ .

**27. Standard Copper Sulphate.**

Dissolve 3.847 grams of pure  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in water, add a few drops of  $\text{H}_2\text{SO}_4$  and dilute to one litre. One cc. will contain 0.001 grams of copper.

**28. Standard  $\text{KMnO}_4$  Solution for  $\text{CaO}$ .**

Dissolve 12.974 grams of  $\text{KMnO}_4$  in 2300 cc. of water. One cc. equals 1 per cent. of  $\text{CaO}$  where 0.500 grams of the substance are taken for analysis. The solution is standardized with an oxalic acid solution containing 5.615 grams per half litre of water.

**29. Reagents for the Cyanide Assay.**

(a) *Standard 1% Potassium Cyanide.*—Weigh carefully 10 grams of c. p. potassium cyanide, dissolve and dilute to 1 litre with distilled water.

(b) *Standard Silver Nitrate.*—Weigh accurately 6.45 grams of c. p. silver nitrate, dissolve and dilute to 1 litre with distilled water.

Compare these solutions as follows:—

With a pipette draw off 10 cc. of the standard KCN solution, dilute with distilled water to about 40 cc., and run in the  $\text{AgNO}_3$  solution, from a burette, until one drop produces a faint permanent precipitate. If the KCN solution contains exactly 1 per cent. of potassium cyanide, 20 cc. of the  $\text{AgNO}_3$  solution will be required. Label the bottle containing the KCN solution, and mark on it its exact strength in pounds and 1/10th pounds of potassium cyanide per ton.

(c) *Standard Silver Nitrate.*—Dissolve 6.450 grams of

pure  $\text{AgNO}_3$  in one litre of water. One cc. of this solution equals one pound of pure cyanide of potassium in 2000 pounds of solution, taking for the test 10 cc. of the liquid to be tested for cyanide strength.

(d) *Standard Solution of KCN*.—Dissolve 1.500 grams of pure potassium cyanide in 100 cc. of water, making a  $1\frac{1}{2}$  per cent. solution. In making the solution determine the per cent. of actual KCN in the salt used, since the commercial article never contains 100 per cent.

### 30. Reagents Used in Water Analysis.

(a) *Silver Nitrate Solution*.—Dissolve 4.7974 grams of pure  $\text{AgNO}_3$  in one litre of water. One cc. of this solution will precipitate 0.001 grams of chlorine.

(b) *Potassium Chromate Indicator*.—Make a cold saturated solution in water. It must be free from chlorine.

(c) *N/100 Iodine*.—Place 1.2685 grams of re-sublimed iodine and 1.800 grams of KI in a graduate and dilute to exactly 1 litre. Be sure that the iodine is all dissolved before using.

(d) A strong solution of  $\text{BaCl}_2$ .

(e) A saturated solution of ammonium chloride.

(f) A solution of  $\text{Ba}(\text{OH})_2$ , accurately titrated with n/10 acid.

(g) Of pure  $\text{Na}_2\text{CO}_3$  1.061 grams are dissolved in water and diluted to 1 litre. One cc. = 0.001061 grams of  $\text{Na}_2\text{CO}_3$  or, 0.00101 grams of  $\text{CaCO}_3$ .

(h) A standard solution of  $\text{H}_2\text{SO}_4$  is prepared by adding 1 cc. of strong acid to 1 litre of water. This solution should be titrated with Reagent 30-g, using lacmoid or phenacetolin indicator with heat until the solutions are ex-

### 31. Reagents for Zinc Titration.

(a) Dissolve 200 grams of  $\text{NH}_4\text{Cl}$  in a mixture of 500 cc. of strong ammonia and 350 cc. of water.

(b) *Standard Potassium Ferro-Cyanide.*—Dissolve 22 grams of potassium ferro-cyanide in water and dilute to 1 litre. Standardize as follows: Weigh carefully about 0.100 grams of pure zinc, and dissolve in 6 cc. of strong HCl, using a 400 cc. beaker. Add about 10 grams of  $\text{NH}_4\text{Cl}$  and 200 cc. of boiling water, and titrate with the ferro-cyanide solution until one drop, when tested on a porcelain plate with a drop of a strong solution of uranium nitrate, shows a brown tinge. About 20 cc. of the ferro-cyanide will be required; hence, nearly this amount may be run in rapidly, before making the test, and the titration then carefully finished by testing after each additional drop. Instead of using a single drop of the zinc solution for the test, the reaction is much sharper if several drops are placed in a depression in the plate and tested with a single drop of a strong uranium solution. As this is near the end of the titration, the zinc thereby lost is insignificant. As soon as a brown tinge is obtained, note the reading of the burette, then wait a minute or two and observe if one or more of the preceding tests do not also develop a tinge. The end-point is usually passed by a test or two, and the burette reading must be accordingly corrected. A further correction must be made for the amount of ferro-cyanide required to produce a tinge under the same conditions when no zinc is present. This is only one or two drops. One cc. of the standard solution of ferro-cyanide will equal about 0.005 grams of zinc, or about 1 per cent. when a 0.500 gram sample is taken.

### 32. Reagents for Phosphate Analysis.

(a) *Ammonium Citrate Solution*.—Mix 370 grams of commercial citric acid with 1½ litres of water; nearly neutralize with commercial ammonia, cool, exactly neutralize with  $\text{NH}_4\text{OH}$  (testing with a saturated alcoholic solution of corallin) and make the volume 2 litres. The specific gravity, at 20° C., should be 1.09.

(b) *Molybdate Solution*.—Dissolve 100 grams of molybdic acid in 417 cc. of  $\text{NH}_4\text{OH}$  (sp. gr. 0.96) and pour this solution into 1250 cc. of  $\text{HNO}_3$  (sp. gr. 1.20). Keep the mixture in a warm place for several days, or until a portion heated to 40° C. deposits no yellow precipitate. Decant the solution from any sediment, and preserve in glass-stoppered vessels.

(c) *Ammonium Nitrate Solution*.—Dissolve 200 grams of  $\text{NH}_4\text{NO}_3$  in water, and dilute to 2 litres.

(d) *Magnesia Mixture*.—Dissolve 22 grams of recently ignited calcined magnesia in dilute HCl, avoiding an excess; add a slight excess of calcined magnesia, boil to precipitate iron, alumina and phosphoric acid, filter, add 280 grams of  $\text{NH}_4\text{Cl}$ , 700 cc. of  $\text{NH}_4\text{OH}$  (sp. gr. 0.96), and water to bring the volume to 2 litres. Instead of 22 grams of calcined magnesia, 110 grams of crystallized magnesium chloride may be used.

(e) *Dilute Ammonia*.—This solution should contain 2.5 per cent. of  $\text{NH}_3$ .

(f) *Magnesium Nitrate Solution*.—Dissolve 320 grams of calcined magnesia in  $\text{HNO}_3$ , avoiding an excess of the latter; add a little calcined magnesia in excess, boil, filter, and dilute with water to 2 litres.

### 33. Standard Ammonium Molybdate, for Lead.

(a) Dissolve 9 grams of  $\text{NH}_4\text{MoO}_4$  in 1 litre of water, with the addition of a few drops of  $\text{NH}_4\text{OH}$  if necessary to clarify the solution.

Standardize this solution as follows: Dissolve 0.300 grams of pure  $\text{PbSO}_4$  in hot  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ , acidify with acetic acid and dilute with hot water to 250 cc.; heat to boiling and add the molybdate solution till all of the lead is precipitated, and an excess of molybdate is indicated by the yellow color produced in a drop of tannin solution on a porcelain slab. The 0.300 grams of  $\text{PbSO}_4$  contain 0.204876 grams of lead, and each cc. of the above molybdate solution should equal about 0.010 grams of lead.

(b) *Tannin Indicator.*—Dissolve 1 gram of tannin in 300 cc. of water. Use it in drops on a porcelain slab.

### 34. Standard KCN Solution, for Copper.

Dissolve 60 grams of KCN in 1 litre of water. To standardize, dissolve 0.300 grams of pure copper foil in 5 cc. of strong  $\text{HNO}_3$ , heat till nitrous fumes no longer appear, dilute slightly, add 10 cc. of strong  $\text{NH}_4\text{OH}$ , cool and titrate with the KCN solution. When the end approaches, dilute the copper solution to 180 cc. and finish the titration carefully. Each cc. of the KCN solution should be made to correspond to 0.005 grams of copper. The solution should be kept in a dark-colored bottle, protected from light, and the solution covered with a layer of coal-oil.

It should be titrated against pure copper, as above, before using, taking *in all cases* a similar tint for the end reaction.

### 35. Precipitated Barium Carbonate.

To a boiling solution of pure  $\text{BaCl}_2$  add gradually a solution of pure ammonium carbonate, till all of the barium is precipitated. Wash thoroughly with water till the washings (acidulated with  $\text{HNO}_3$ ) show no reaction with silver nitrate.

### 36. Volumetric Sulphur in Coal or Coke.

In this method, upon the addition of barium chromate to the solution containing sulphuric acid, barium sulphate is precipitated and chromic acid is set free. After making alkaline and addition of potassium iodide, the chromic acid is reduced and iodine is set free, according to the following equation:—  $(\text{NH}_4)_2\text{CrO}_4 + 3 \text{ KI} + 8 \text{ HCl} = \text{CrCl}_3 + 2 \text{ NH}_4\text{Cl} + 3 \text{ I} + 3 \text{ KCl} + 4 \text{ H}_2\text{O}$ . The barium chromate is made by uniting dilute solutions of barium chloride and potassium chromate, the weights of the two ingredients being based upon the molecular weights (242.316 and 246.5 respectively); the precipitated barium chromate is then filtered and washed thoroughly. The solution of barium chromate is made by dissolving 23 grams of the pure salt in a mixture of 80 cc. of concentrated hydrochloric acid and 920 cc. of water.

### 37. Reagents for Arsenic Determination.

(a) *Cupric Chloride Solution*.—Dissolve 300 grams of pure  $\text{CuCl}_2$  in 1 litre of  $\text{HCl}$  of sp. gr. 1.20, and mix this solution with 1 litre of a solution of zinc chloride, which boils at  $180^\circ \text{ C}$ . The zinc solution is made by adding successively to 1 pound of pure stick zinc 500 cc. of water and

1250 cc. of HCl of sp. gr. 1.20; when the zinc is in solution, bring to a boil and evaporate a little to bring the boiling-point up to 180° C., thus making about 1,100 cc. of solution.

(b) *Standard Iodine Solution.*—This is best made so that 1 cc. is equal to about 0.005 grams of arsenic. Dissolve about 40 grams of KI in a minimum of water, and to this add 17 grams of iodine. After complete solution of the iodine, dilute to 1 litre with distilled water.

To standardize, dissolve 0.300 grams of c. p. As<sub>2</sub>O<sub>3</sub> in a little KOH or NaOH, dilute to about 200 cc., acidify slightly with HCl, add about 2 grams of NaHCO<sub>3</sub>, some starch solution and titrate to a permanent blue. Pure arsenious acid contains 75.757 per cent. of arsenic. A check should be made by precipitating with H<sub>2</sub>S the same amount of arsenic as that used in standardizing, filtering off the sulphide and distilling as in the method given. This may supply a correction factor, since the As<sub>2</sub>O<sub>3</sub> used may not be strictly pure and the cupric chloride frequently contains arsenic.

### 38. Reagents in Thio-cyanate-Iodide Copper Method.

- (a) Ammonium thio-cyanate, 100 grams per litre of water.
- (b) Sodium thio-sulphate, about 19.5 grams per litre of water.
- (c) Potassium iodide, a 50 per cent solution.
- (d) Starch solution. About 0.500 grams of starch is boiled with 20 cc. of water, diluted with 150 cc. of hot water and allowed to cool and settle. The clear solution is used.

The thio-sulphate is standardized against pure copper. About 0.20 grams of the copper are dissolved in 5 cc. of

dilute nitric acid; 50 cc. of water are added, and the solution is boiled till red fumes are completely expelled. Add a very slight excess of ammonia, and again boil; acidify with acetic acid and cool. When cold, add 6 cc. of potassium iodide solution, agitate, and titrate with sodium thio-sulphate solution until the brown color of the iodine is barely visible; add 2 to 3 cc. of starch solution, and titrate to a cream color.

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### USEFUL TABLES.

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#### Number and Capacities of Beakers.

The so-called "usual form" of beaker is made either with or without a lip; the numbers with corresponding capacities are as follows:

Number .....	00	0	1	2	3	4	5	6	7	8	9	10	11	12
Capacity .....	1	2	3	5	9	13	18	26	34	46	64	76	96	120

ounces.

"Griffin" Beakers are the low, wide form and are numbered as follows:

Number .....	00	0	1	2	3	4	5	6	7	8	9	10	11	12
Capacity .....	1	2	5	8	12	20	25	40	50	64	75	96	112	128

ounces.

(See table for the conversion of fl. ounces to cc.)

#### Conversion of Metric and English Weights and Measures.

Cu. Inches to cc. Cc. to cu. in. Fl. ounces to cc. Grains to Grams.

1 = 16.386	1 = 0.06103	1 = 28.396	1 = 0.06479
2 = 32.772	2 = 0.12206	2 = 56.792	2 = 0.12958
3 = 49.158	3 = 0.18309	3 = 85.188	3 = 0.19437
4 = 65.544	4 = 0.24412	4 = 113.584	4 = 0.25916
5 = 81.930	5 = 0.30515	5 = 141.980	5 = 0.32395
6 = 98.316	6 = 0.36618	6 = 170.376	6 = 0.38874
7 = 114.702	7 = 0.42721	7 = 198.772	7 = 0.45353
8 = 131.088	8 = 0.48824	8 = 227.168	8 = 0.51832
9 = 147.474	9 = 0.54927	9 = 255.564	9 = 0.58311

Grams to Grains.	16 drachms = 1 ounce = 437.5 grains Avdp. Wt.
1 = 15.43235	16 ounces = 1 pound = 7000 grains Avdp. Wt.
2 = 30.86470	20 pennyweights = 1 ounce = 480 grains Troy Wt.
3 = 46.29705.	12 ounces = 1 pound = 5760 grains Troy Wt.
4 = 61.72940	Pounds Avdp. $\times$ 0.82286 = Pounds Troy.
5 = 77.16175	Pounds Troy $\times$ 1.2153 = Pounds Avdp.
6 = 92.59410	Ounces Avdp. $\times$ 0.9114 = Ounces Troy.
7 = 108.02645	Ounces Troy $\times$ 1.097 = Ounces Avdp.
8 = 123.45880	20 fluid ounces = 1 pint. (Apoth. Fl. Meas.)
9 = 138.89115	8 pints = 1 gallon. (Apoth. Fl. Meas.)
	1 gallon = 277.27384 cubic in. (Apoth. Fl. Meas.)
	1 gallon, U. S Standard, = 231 cubic inches.

### Conversion Tables.

To convert degrees of Twaddle's hydrometer into specific gravity (water = 1000) multiply by 5 and add 1000.

To convert specific gravity (water = 1000) into degrees of Twaddle's hydrometer, subtract 1000 and divide by 5.

To convert sp. gr. (Air = 1) to sp. gr. (H = 1) multiply by 14.438.

To convert sp. gr. (H = 1) to sp. gr. (Air = 1) multiply by 0.06926.

To convert grams per litre into grains per gallon multiply by 58.318.

To convert grains per gallon into grams per litre, multiply by 0.017164.

To convert parts per 100,000 into grains per gallon, multiply by 0.58318.

To convert grains per gallon into parts per 100,000, divide by 0.58318.

**Specific Gravities Corresponding to Degrees of Baume's Hydrometer.**

*Liquids Heavier than Water.*

B.	Sp. Gr.	B.	Sp. Gr.	B	Sp. Gr.	B.	Sp. Gr.
0.	1.000	19.	1.152	38.	1.357	57.	1.652
1.	1.007	20.	1.161	39.	1.370	58.	1.671
2.	1.014	21.	1.171	40.	1.383	59.	1.691
3.	1.022	22.	1.180	41.	1.397	60.	1.711
4.	1.029	23.	1.190	42.	1.410	61.	1.732
5.	1.036	24.	1.199	43.	1.424	62.	1.753
6.	1.044	25.	1.210	44.	1.438	63.	1.774
7.	1.052	26.	1.221	45.	1.453	64.	1.796
8.	1.060	27.	1.231	46.	1.468	65.	1.819
9.	1.067	28.	1.242	47.	1.483	66.	1.846
10.	1.075	29.	1.253	48.	1.498	67.	1.872
11.	1.083	30.	1.264	49.	1.514	68.	1.897
12.	1.091	31.	1.275	50.	1.530	69.	1.921
13.	1.100	32.	1.286	51.	1.546	70.	1.946
14.	1.108	33.	1.297	52.	1.563	71.	1.974
15.	1.116	34.	1.309	53.	1.580	72.	2.000
16.	1.125	35.	1.320	54.	1.597	73.	2.031
17.	1.134	36.	1.332	55.	1.615	74.	2.059
18.	1.143	37.	1.345	56.	1.634		

*Liquids Lighter than Water.*

B.	Sp. Gr.	B.	Sp. Gr.	B	Sp. Gr.	B.	Sp. Gr.
10.	1.000	23.	0.918	36.	0.849	49.	0.789
11.	0.993	24.	0.913	37.	0.844	50.	0.785
12.	0.986	25.	0.907	38.	0.839	51.	0.781
13.	0.980	26.	0.901	39.	0.834	52.	0.777
14.	0.973	27.	0.896	40.	0.830	53.	0.773
15.	0.967	28.	0.890	41.	0.825	54.	0.768
16.	0.960	29.	0.885	42.	0.820	55.	0.764
17.	0.954	30.	0.880	43.	0.816	56.	0.760
18.	0.948	31.	0.874	44.	0.811	57.	0.757
19.	0.942	32.	0.869	45.	0.807	58.	0.753
20.	0.936	33.	0.864	46.	0.802	59.	0.749
21.	0.930	34.	0.859	47.	0.798	60.	0.745
22.	0.924	35.	0.854	48.	0.794		

**Comparison of Thermometer Scales of Centigrade, Fahrenheit and Reaumur.**

C. Water freezes at  $0^{\circ}$  F. Water freezes at  $32^{\circ}$  R. Water freezes at  $0^{\circ}$   
 C. Water boils at  $100^{\circ}$  F. Water boils at  $212^{\circ}$  R. Water boils at  $80^{\circ}$

### Conversion of Thermometer Degrees.

Fahrenheit to Centigrade, subtract 32, multiply by 5, divide by 9.

Fahrenheit to Reaumur, subtract 32, multiply by 4, divide by 9.

Centigrade to Fahrenheit, multiply by 9, divide by 5, and add 32.

Centigrade to Reaumur, multiply by 4, divide by 5.

Reaumur to Fahrenheit, multiply by 9, divide by 4, add 32.

Reaumer to Centigrade, multiply by 5, divide by 4.

### Comparison of Various Measures.

	Cubic-In.	Grains Water at 62° F.	Cubic Centimeters.
1 English Imperial, gallon . . . .	= 277.274	= 70,000.00	= 4,543.000
1 English Wine or Worcester gallon . . . . .	= 231.0	= 58,318.00	= 3,785.2
1 English Corn gallon. . . . .	= 268.0	= 67,861.00	= 4,402.9
1 English Ale gallon. . . . .	= 282.0	= 71,193.40	= 4,619.2

### Liquid or Wine Measure, U. S. Standard.

The standard unit of Liquid Measure adopted by the U. S. Government is the Winchester Wine Gallon, which contains 231 cubic inches, and holds 8.339 pounds avoirdupois of distilled water, at its maximum density weighed in air, the barometer being at 30 inches.

Tun	Pipe.	H'head.	Gallons	Quarts	Pints.	Gills.	Cubic In.	Cu. cm
1	=	2	=	4	=	252	=	1008
	1	=	2	=	126	=	504	=
		1	=	63	=	252	=	1008
			1	=	4	=	8	=
				1	=	2	=	32
					1	=	8	=
						1	=	57.75
							4	=
								28.875 =
								473.11

A gallon of water (U. S. Standard) weighs 8 1/3 pounds, and contains 231 cubic inches.

A cubic foot of water weighs 62½ pounds, and contains 1,728 cubic inches, or 7½ gallons.

### Dimensions of Cylinders in Inches, Holding Approximately the below-named U. S. Standard Measures.

A cylinder	Dia.	Height.	contains approximately	1 gill	U. S. Standard.
"	1 1/2"	— 3"	"	1/4 pint	" "
"	2 1/2	— 3 1/2	"	1 pint	" "
"	3 1/2	— 3	"	1 quart	" "
"	3 1/2	— 6	"	1 gallon	" "
"	7	— 6	"	8 gallons	" "
"	14	— 12	"	10 gallons	" "
"	14	— 15	"		

### Dry Measure.

Bush el.	Pecks.	Gallons.	Quarts.	Pints.	Cu. Inch
1	=	4	=	8	537.6
		1	=	2	268.8
			=	1	67.2
			=	2	33.6
			=	1	

NOTE.—The standard U. S. bushel is the Winchester bushel, which is in cylinder form, 18½ inches diameter and 8 inches deep, and contains 2,150.42 cubic inches.

The English Imperial bushel ..... =  $\left\{ \begin{array}{l} 2218.192 \text{ cubic inches.} \\ 1.03152 \text{ U. S. bushels.} \end{array} \right.$

The English Quarter..... =  $\left\{ \begin{array}{l} 8 \text{ Imperial bushels.} \\ 8\frac{1}{4} \text{ (nearly) U. S. bushels.} \\ 10.2694 \text{ cubic feet.} \end{array} \right.$

### Linear Measure, U. S. Standard.

The standard unit of the United States and British linear measure is the yard. It was intended to be exactly the same for both countries, but in reality the United States' yard exceeds the British standard by .00087 inch. The actual standard of length for the United States is a brass scale 82 inches long, prepared for the Coast Survey and deposited in the office of Weights and Measures at the U. S. Treasury Department, Washington. The yard is between the 27th and 63d inches of this scale. The temperature at which this scale is designed to be standard, and at which it is used in the U. S. Coast Survey, is 62° Fahrenheit.

## Physical Constants of Various Metals.

Metals.	Symbol.	Atomic Weight.	Specific Gravity.	Specific Heat.	Melting Points.	
					Deg. C.	Deg. F.
Aluminum.....	Al	27.1	2.56	0.212	700	1292
Antimony.....	Sb	120.2	6.71	0.051	432	809
Arsenic*.....	As	75.	5.67	0.061	.....	.....
Barium.....	Ba	137.4	3.75	0.047	1200	2192
Bismuth.....	Bi	208.5	9.80	0.081	258	496
Cadmium.....	Cd	112.4	8.60	0.057	320	608
Cæsium.....	Cs	133.	1.88	.....	26	78
Calcium.....	Ca	40.1	1.57	0.170	.....	Red heat
Chromium.....	Cr	52.1	6.80	0.120	.....	.....
Cobalt.....	Co	59.	8.50	0.110	1600	2912
Copper.....	Cu	63.6	8.82	0.094	1050	1922
Didymium.....	Di	146.8	6.54	0.046	.....	.....
Glucinum.....	Gl	9.1	2.07	0.580	.....	.....
Gold.....	Au	197.2	19.32	0.032	1102	2016
Indium.....	In	114.	7.42	0.057	176	348
Iridium.....	Ir	198.	22.43	0.083	2500	4532
Iron.....	Fe	55.9	7.86	0.110	1600	2912
Iron, Cast.....	.....	.....	7.1	.....	1530	2786
Iron, Wrought.....	.....	.....	7.6 7.8	.....	1808	3286
Lanthanum.....	La	138.9	6.20	0.045	.....	.....
Lead.....	Pb	206.9	11.37	0.031	322	612
Lithium.....	Li	7.03	0.59	0.941	180	356
Magnesium.....	Mg	24.36	1.74	0.250	750	1382
Manganese.....	Mn	55.	8.00	0.120	1650	3002
Mercury†.....	Hg	200.	13.59	0.032	40	104
Molybdenum.....	Mo	96.	8.60	0.072	.....	.....
Nickel.....	Ni	58.7	8.80	0.110	1537	2799
Niobium.....	Nb	94.	6.27	.....	.....	.....
Osmium.....	Os	191.	22.48	0.031	2500	4532
Palladium.....	Pd	106.5	11.50	0.059	1500	2732
Platinum.....	Pt	194.8	21.50	0.033	1808	3286
Potassium.....	K	39.15	0.87	0.170	62	143
Rhodium.....	Rh	103.	12.10	0.058	2000	3632
Rubidium.....	Rb	85.4	1.52	0.077	38	100
Ruthenium.....	Ru	101.7	12.26	0.061	1800	3272
Silver.....	Ag	107.93	10.53	0.056	1023	1873
Sodium.....	Na	23.05	0.97	0.290	95	203
Steel.....	.....	.....	7.8-7.9	.....	1808	3286
Strontium.....	Sr	87.6	2.54	0.074	.....	.....
Tantalum.....	Ta	183.	10.80	.....	.....	.....
Tellurium.....	Te	127.6	6.25	0.047	595	977
Thallium.....	Tl	204.1	11.85	0.084	268	550
Thorium.....	Th	232.5	7.70	0.088	.....	.....
Tin.....	Sn	119.	7.29	0.056	228	442
Titanium.....	Ti	48.1	.....	0.130	.....	.....
Tungsten.....	W	184.	19.10	0.038	.....	.....
Uranium.....	U	238.5	18.70	0.028	.....	.....
Vanadium.....	V	51.2	5.50	.....	.....	.....
Zinc.....	Zn	65.4	7.15	0.094	411	772
Zirconium.....	Zr	90.6	4.15	0.066	.....	.....

\* Arsenic volatilizes at 356° C.

† Mercury volatilizes at 360° C.

### Factors for Computation of Results.

**NOTE.**—In the use of these factors it should be remembered that they are computed from the Table of Atomic Weights, and in any "check" analyses comparison should be made, *in all cases*, of the atomic weights used by the different chemists employed.

Sought	Found.	Factor.	Sought	Found.	Factor.
Al.....	Al <sub>2</sub> O <sub>3</sub> .....	0 5303	FeO.....	Fe.....	1 2862
Al.....	AlPO <sub>4</sub> .....	0 2219	Pb.....	PbO.....	0 9222
NH <sub>3</sub> .....	NH <sub>4</sub> Cl.....	0 3188	Pb.....	PbSO <sub>4</sub> .....	0 6829
NH <sub>3</sub> .....	2NH <sub>4</sub> Cl, PtCl <sub>4</sub> .....	0.0769	Pb.....	PbS.....	0 8658
Sb.....	Sb <sub>2</sub> O <sub>3</sub> .....	0.8835	Li <sub>2</sub> O.....	Li <sub>2</sub> O <sub>3</sub> .....	0.4058
Sb.....	Sb <sub>2</sub> O <sub>5</sub> .....	0.7897	Li <sub>2</sub> O.....	Li <sub>2</sub> SO <sub>4</sub> .....	0 2729
Sb.....	Sb <sub>2</sub> S <sub>3</sub> .....	0.7142	Li <sub>2</sub> O.....	Li <sub>3</sub> PO <sub>4</sub> .....	0.3884
As.....	Mg <sub>2</sub> As <sub>2</sub> O <sub>7</sub> .....	0.4827	Mg.....	MgO.....	0.6035
As.....	MgNH <sub>4</sub> AsO <sub>4</sub> .....	0 4133	MgO.....	MgSO <sub>4</sub> .....	0.3351
As.....	As <sub>2</sub> O <sub>3</sub> .....	0 7575	MgO.....	Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> .....	0.3624
As.....	As <sub>2</sub> S <sub>3</sub> .....	0 6093	Mn.....	MnO.....	0 7746
As.....	As <sub>2</sub> O <sub>5</sub> .....	0.6521	Mn.....	Mn <sub>3</sub> O <sub>4</sub> .....	0.7205
As.....	Ag <sub>3</sub> AsO <sub>4</sub> .....	0.1820	Mn.....	Mn <sub>3</sub> O <sub>4</sub> .....	0.6962
BaO.....	BaSO <sub>4</sub> .....	0 6571	MnO.....	MnSO <sub>4</sub> .....	0 4700
Ba.....	BaSO <sub>4</sub> .....	0 5885	Mn.....	Mn <sub>2</sub> P <sub>2</sub> O <sub>7</sub> .....	0.3873
BaO.....	BaF <sub>2</sub> SiF <sub>4</sub> .....	0.5468	MnO.....	Mn <sub>2</sub> P <sub>2</sub> O <sub>7</sub> .....	0 5000
BaO.....	BaCO <sub>3</sub> .....	0 7750	MnO.....	MnS.....	0.8155
Bi.....	Bi <sub>2</sub> O <sub>3</sub> .....	0 8967	Hg.....	Hg <sub>2</sub> Cl <sub>2</sub> .....	0 8494
B.....	B <sub>2</sub> O <sub>3</sub> .....	0.8142	Hg.....	HgO <sub>2</sub> .....	0.7882
Br.....	AgBr.....	0 4255	Hg.....	HgS.....	0.8618
Ca.....	CaO.....	0 7147	MoO <sub>3</sub> .....	(NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub> , 11MoO <sub>3</sub> .....	0.9135
CaO.....	CaCO <sub>3</sub> .....	0.5804	Ni.....	NiO.....	0.7858
CaO.....	CaSO <sub>4</sub> .....	0 4120	N.....	2NH <sub>4</sub> Cl, PtCl <sub>4</sub> .....	0.0633
CaCO <sub>3</sub> .....	CaSO <sub>4</sub> .....	0.7351	P.....	P <sub>2</sub> O <sub>5</sub> .....	0.4366
C.....	CO <sub>2</sub> .....	0.2727	P <sub>2</sub> O <sub>5</sub> .....	Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> .....	0.6375
CO <sub>2</sub> .....	CaCO <sub>3</sub> .....	0.4395	P.....	Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> .....	0.2783
Cl.....	AgCl.....	0.2472	P.....	(NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub> , 11MoO <sub>3</sub> .....	0.01796
Cr.....	Cr <sub>2</sub> O <sub>3</sub> .....	0.6846	P <sub>2</sub> O <sub>5</sub> .....	Ag <sub>3</sub> P <sub>2</sub> O <sub>7</sub> .....	0 2844
CrO <sub>3</sub> .....	Cr <sub>2</sub> O <sub>3</sub> .....	1.3153	K.....	K <sub>2</sub> O.....	0.8303
CrO <sub>3</sub> .....	PbCrO <sub>4</sub> .....	0.8099	K <sub>2</sub> O.....	2KCl, PtCl <sub>4</sub> .....	0.1941
CoO.....	Co.....	1.2712	Si.....	SiO <sub>2</sub> .....	0.4702
Co.....	CoSO <sub>4</sub> .....	0 3805	Ag.....	AgCl.....	0.7527
Co.....	Co <sub>3</sub> O <sub>4</sub> .....	0 7344	Na.....	Na <sub>2</sub> O.....	0.7423
CoO.....	Co <sub>2</sub> O <sub>3</sub> , 3K <sub>2</sub> O, {	0.2126	Na.....	NaCl.....	0.3958
CoO.....	5NiO <sub>3</sub> , 2H <sub>2</sub> O, }		Na <sub>2</sub> O.....	Na <sub>2</sub> CO <sub>3</sub> .....	0.5852
CoO.....	2CoSO <sub>4</sub> , 3K <sub>2</sub> SO <sub>4</sub> ..	0.1800	Na <sub>2</sub> O.....	NaHCO <sub>3</sub> .....	0.2742
Co.....	CoO.....	0.7867	SrO.....	SrCO <sub>3</sub> .....	0.7019
Cu.....	CuO.....	0.7989	Sr.....	SrO.....	0 8455
Cu.....	Cu <sub>2</sub> O.....	0.8882	S.....	BaSO <sub>4</sub> .....	0.1373
Cu.....	Cu <sub>2</sub> S.....	0.7987	SO <sub>3</sub> .....	BaSO <sub>4</sub> .....	0.3428
F.....	CaF <sub>2</sub> .....	0.4865	SO <sub>4</sub> .....	BaSO <sub>4</sub> .....	0 4114
F.....	SiF <sub>4</sub> .....	0.7279	S.....	PbSO <sub>4</sub> .....	0.1058
I.....	AgI.....	0.5402	Sn.....	SnO <sub>2</sub> .....	0.7880
I.....	PdI <sub>2</sub> .....	0.7043	SnO.....	SnO <sub>2</sub> .....	0.8940
Fe.....	FeO.....	0.7774	Tl.....	TiO <sub>2</sub> .....	0.8005
Fe.....	Fe <sub>2</sub> O <sub>3</sub> .....	0.6996	Zn.....	ZnO.....	0.8084
Fe.....	FeS.....	0.6355	Zn.....	ZnS.....	0.6710

### Indicators.

*Cochinchal Solution.*—This indicator is most useful in titrating solutions of the alkalies and alkaline earths. It is inapplicable in presence of iron or alumina compounds or acetates; it is of a yellowish red color, and is turned violet by alkalies; mineral acids restore the color. The color is not very much modified by  $\text{CO}_2$ . The solution is made by digesting 1 part of powdered cochineal in 10 to 25 parts of alcohol. It may be used in the gas-light.

*Methyl Orange.*—This indicator is used for determining caustic fixed alkalies, titrating mineral acids in the cold, and is very useful for ammonia and its salts. It is inapplicable for hot liquids and organic acids, and is indifferent to  $\text{H}_2\text{S}$  and  $\text{CO}_2$  in the cold. The color is pink with excess of acids, faint yellow with excess of alkali. The solution is made 1 gram per litre of water.

*Litmus Solution.*—A solution of commercial litmus is rendered pink or red by acids, and is changed to the original blue by excess of alkali. Free  $\text{CO}_2$  interferes with the production of the blue color. Litmus cannot be used by gas-light.

, *Phenacetolin.*—A solution of 2 grams per litre of alcohol is used in titrating KOH or NaOH in presence of  $\text{K}_2\text{CO}_3$  or  $\text{Na}_2\text{CO}_3$ , or CaO in presence of  $\text{CaCO}_3$ . Its color is pink with alkalies and yellow with acids.

*Rosolic Acid.*—A solution of 2 grams in 1 litre of 50 per cent. alcohol makes a good indicator for all mineral acids, but is unreliable for organic acids. The yellow color is turned red by alkalies. Formula ( $\text{C}_{20}\text{H}_{18}\text{O}_3$ ).

*Phenol-phthalein.*—A solution of 1 gram in a litre of 50 per cent. alcohol is especially useful in titrating all organic

acids, also fixed caustic alkalies in presence of carbonates. It gives no color with bi-carbonates and is absolutely useless for the titration of free ammonia and its compounds, or for the fixed alkalies when salts of ammonia are present. Purple in alkaline solutions, rendered colorless by acids, Formula ( $C_{20}H_{14}O_4$ ).

*Normal Potassium Chromate.*—The salt must be free from chlorine. Make a cold saturated solution in water. It can only be used with neutral solutions and in titrating chlorine in chlorides.

*Fluorescin.*—A very dilute alcoholic solution of this substance is of much value in titrating colored solutions, in which the addition of the indicator produces a green fluorescence, which is destroyed by free acids.

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